Polymeric Thermotropic Materials for Overheating Protection of Solar Collectors

Dissertation

Katharina Resch

submitted to

University of Leoben
Leoben, Austria

October 2008

Academic Advisor:
O. Univ.-Prof. Dr. Reinhold W. Lang
University of Leoben, Leoben, Austria

Supervisor:
Ao. Univ.-Prof. Dr. Gernot M. Wallner
University of Leoben, Leoben, Austria

Referees:
O. Univ.-Prof. Dr. Reinhold W. Lang
University of Leoben, Leoben, Austria

Prof. Dr. Volker Wittwer
Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany

I declare in lieu of oath, that I wrote this dissertation and performed the associated research myself, using only the support indicated in the acknowledgements and literature cited.

Leoben, October 2008 Katharina Resch

The research work of this dissertation was performed at the Polymer Competence Center Leoben GmbH within the framework of the Non-K$_{plus}$ Program.

The research work of this dissertation was funded by the State Government of Styria, Department *Zukunftsfonds Steiermark*.

ZUKUNFTSfonds STEIERMARK

Das Land Steiermark

ACKNOWLEDGEMENTS

In performing this dissertation I have been accompanied and supported by many people. It is a pleasant aspect that I have now the opportunity to express my gratitude to all of them.

First and foremost I would like to thank my supervisor O. Univ.-Prof. Dr. Reinhold W. Lang, Head of the Institute of Materials Science and Testing of Plastics at the University of Leoben and former Scientific Manager of the Polymer Competence Center Leoben GmbH (PCCL), for offering me the possibility to compose this thesis and the fruitful discussions. It is a privilege to enjoy his guidance and assistance in writing a dissertation.

My thanks go to Prof. Dr. Volker Wittwer (Fraunhofer Institute for Solar Energy Systems) for undertaking the task of being my second referee for this dissertation.

I would like to express my heartfelt gratitude to Ao. Univ.-Prof. Dr. Gernot M. Wallner (Institute of Materials Science and Testing of Plastics at the University of Leoben) for his support throughout the years. To merely say I learned from him the fundamental principles of scientific working and writing would be a gross understatement. He offered me entirely freedom in my research work, always trusted in my abilities, encouraged me in doubtful situations, and never shied away from discussions.

Special thanks go to Dipl.-Ing. Robert Hausner (AEE-Institute for Sustainable Technologies). It was a great pleasure to work with him and learn from him all the important aspects of solar thermal engineering. He was my primary contact for all solar energy related questions and provided the theoretical modeling work for collector systems in our project.

I had the pleasure to supervise and work with Sonja Kahr, Marlene Knausz, Alexander Lovas, and Andreas Weber who participated in our project and have been beneficial for this thesis.

Thanks go to Dipl.-Ing. Michael Buder-Stroisznigg (Polymer Competence Center Leoben GmbH), who shared his knowledge on thermo-mechanical analysis of polymers with me.

I would like to thank Dr. Elisabeth Ingolic (Austrian Centre for Electron Microscopy and Nanoanalysis) for the preparation of samples for high resolution microscopy. Furthermore, my thanks go to Ao. Univ.-Prof. Dr. Christian Teichert (Institute of Physics at the University of Leoben) for discussion of results obtained by Atomic Force Microscopy.

I wish to express my acknowledgements to Cytec Surface Specialties (Drogenbos, BE), Sasol Germany GmbH (Hamburg, DE) and Chemson Polymer Additive AG (Arnoldstein, AT), for providing the materials.

I also would like to thank LEO for untiringly providing translation of words into English.

It is a great experience to be part of the research team of the Institute of Materials Science and Testing of Plastics at the University of Leoben and the Polymer Competence Center Leoben GmbH. I would like to thank all my colleagues here for the favorable working atmosphere. Especially I would like to thank my office-mates Jörg Fischer and Markus Wolfahrt for their friendship, pleasant coffee-breaks and lunches, and many thought-provoking impulses also apart from technical discussions.

I would like to thank all my friends heartily for their assistance in all the non-technical aspects of being a doctoral candidate.

I am deeply grateful to my parents, my sisters Maria and Ingrid, and my brother Karl Peter for providing endless love and support to me. To know that they stand behind me, gives me stability, strength, and balance.

Finally I wish to express my deepest gratitude to Ewald, for his love, support, and encouragement, and for the colorful and laughing time together. To be with him is a great gift of life to me.

One.Life.
Dance.It.

ABSTRACT

Polymeric materials offer a significant cost-reduction potential for solar thermal collectors and may thus benefit a broader utilization of solar energy for various heating purposes. However, the long-term service temperature of plastics is limited. Thus, for potential applications of cost-efficient plastics in flat-plate solar collectors an appropriate design including overheating protection is essential. A feasible way to control stagnation temperatures in an all-polymeric solar collector would be the application of thermotropic glazings, which reversibly change their light transmittance from highly transparent to light diffusing upon reaching a certain threshold temperature. Appropriate thermotropic materials were not developed and investigated yet. Thus, the overall objective of this dissertation was to provide basic knowledge on the development and characterization of thermotropic layers for overheating protection purposes in all-polymeric solar collectors. Specific focus was given to the establishment of a fundamental understanding of relationships between the material formulation and structural parameters and the light-shielding properties of thermotropic layers, based on sound principles of polymer physics and materials science as well as solar physics.

For that purpose (1) an evaluation and strength-weakness analysis of existing thermotropic layers produced from polymeric materials concerning their applicability in solar collectors was carried out, (2) thermotropic prototype-layers were developed and designed for solar collector applications considering aspects of polymer physics, (3) thermotropic prototype-layers were characterized as to relevant morphological parameters and performance properties, (4) structure-property relationships between the performance properties and the inner material structure and formulation parameters of thermotropic prototype-layers were established, and (5) the effect of thermotropic prototype-layers on the efficiency of an all-polymeric flat-plate collector was investigated and modeled.

A review on various thermotropic glazing materials with respect to their ability to meet requirements for overheating protection of a solar thermal collector showed that the systems designed so far have to be adapted and optimized for solar collector applications, especially regarding their switching temperatures and long-

term stability. Among different thermofunctional materials, thermotropic systems with fixed domains (TSFD) were observed to possess the highest development potential for overheating protection applications in solar collectors. In TSFD scattering particles (also referred to as additives), which exhibit a sudden change of refractive index upon reaching a threshold temperature, are statically embedded in a matrix material (in general in a thermoset resin).

A methodological approach for the selection of a matrix material appropriate to the production of TSFD was defined, which included the determination of cross-linking parameters (curing rate, degree of cure) and the glass transition temperature of the resin material. Using exemplarily a UV-curable urethane acrylate resin it was shown that applying Dielectric Analysis (DEA), Attenuated Total Reflectance spectroscopy (ATR) and Dynamic Mechanical Analysis (DMA) relevant performance properties of a matrix material can be derived.

For a systematic investigation on TSFD for solar collector applications numerous prototype-layers were prepared by variation of base resin and additive type and concentration. TSFD prototype-layers were characterized concerning solar optical properties of the thermotropic layers in the clear and opaque state, and the switching temperature and transition temperature range. Furthermore differences in refractive index of matrix and additive, additive concentration and scattering domain size, shape and distribution were investigated. The ascertained morphological parameters were related to the light-shielding performance of the layers. Moreover, relationships between properties of formulation ingredients and the switching characteristics of the thermotropic layers were established. The overheating protection performance of the thermotropic layers in an all-polymeric solar collector with twin-wall sheet glazing and black absorber was evaluated applying theoretical modeling.

In the clear state the TSFD prototype-layers exhibited a hemispheric solar transmittance between 76 and 87%, with diffuse fractions ranging from 14 to 71%. Switching from the clear to the scattering state occurred at temperatures between 40 and 80°C. Transition temperature ranges between 10 and 25 K were recorded. Above the switching threshold the hemispheric solar transmittance changed to values ranging between 62 and 85%, with diffuse fractions between 36 and 78%.

Pronounced differences in refractive index >0.04 between matrix and scattering domain above the switching temperature were detected to be advantageous for the light-shielding efficiency of the layers. The most efficient additive concentration for the considered thermotropic layers was observed to be 5 m%. A uniform additive distribution across the film thickness was found to benefit the back-scattering efficiency. Thermotropic layers formulated with additive types exhibiting a short chain length displayed roughly spherical scattering particles with diameters between 0.5 and 3 µm and a moderate reduction in hemispheric solar transmittance along with a significant increase of diffuse solar transmittance. Additive types with long-chain molecules developed anisotropic scattering domains resembling contorted disks with a diameter up to 50 µm and a thickness between 100 and 400 nm. These disk-like scattering features yielded enhanced light-shielding properties.

The highest solar back-scattering efficiency of the TSFD prototype-layers in the opaque state was detected for material types based on resin types which exhibit a higher cross-linking density and low chain segment mobility (high glass transition temperature). Thermotropic layers produced from a resin with a wide-meshed network and low glass transition temperature exhibited the most distinct increases of diffuse solar transmittance above the switching threshold. The light-shielding efficiency of thermotropic layers being formulated with non-polar additive types increased with increasing molecular mass of the additives. The comparison of the additives thermal transitions with the switching characteristics of the thermotropic layer revealed an excellent correlation. This allows for tailoring the switching temperature and transition temperature ranges by selecting adequate additives.

As to the application of the produced TSFD prototype-layers for overheating protection of solar collectors it was found that compared to the use of the functional materials on the absorber, their utilization in the glazing maximized the efficient collector working temperature range and minimized stagnation temperatures. Thermotropic layers were found to reduce the maximum absorber temperatures to values between 129 and 146°C. Stagnation temperatures below 130°C would allow for the application of cost-efficient plastics as absorber materials.

KURZFASSUNG

Durch die Anwendung von Kunststoffen als Komponenten für Sonnenkollektoren zur Warmwasserbereitung und Raumheizung können Kollektorkosten erheblich reduziert werden. Demzufolge haben Kunststoffkollektoren ein hohes Potential für den Breiteneinsatz ohne staatliche Subventionen. Beim Einsatz von Kunststoffen ist jedoch sicherzustellen, dass Kollektorüberhitzungen von über 200°C, die oberhalb der thermischen Langzeitbelastbarkeit von kostengünstigen Kunststoffen liegen, vermieden werden. Dies bedingt ein entsprechendes Kollektordesign, welches insbesondere auch geeignete Überhitzungsschutzeinrichtungen inkludiert. Ein wirksames Mittel zur Temperaturbegrenzung von Kollektoren stellen thermotrope Verglasungen dar, welche bei Erreichen eines Temperaturschwellwerts reversibel von einem transparenten in einen opaken Zustand übergehen. Thermotrope Schichten für Kollektoranwendungen wurden bis dato noch nicht gezielt entwickelt und untersucht. Dementsprechend liegt die Hauptzielsetzung dieser Dissertation in der Erarbeitung und Bereitstellung grundlegender Informationen was die Entwicklung und Charakterisierung thermotroper Schichten für die Anwendung als Überhitzungsschutzelement in Sonnenkollektoren betrifft. Spezielles Augenmerk wurde auf den Aufbau eines fundierten Verständnisses der physikalischen Zusammenhänge zwischen Materialzusammensetzung sowie morphologischer Parameter und den Überhitzungsschutzeigenschaften thermotroper Materialien gelegt.

Dazu wurden (1) bestehende, auf Basis polymerer Werkstoffe hergestellte, thermotrope Materialien hinsichtlich ihrer Eignung für den Einsatz in Sonnenkollektoren evaluiert, (2) thermotrope Prototyp-Schichten für Kollektoranwendungen unter besonderer Berücksichtigung polymerphysikalischer Aspekte konzipiert und entwickelt, (3) thermotrope Prototyp-Schichten hinsichtlich relevanter morphologischer Parameter und Anwendungseigenschaften charakterisiert, (4) Struktur-Eigenschaftskorrelationen zwischen Materialzusammensetzung und den Überhitzungsschutzeigenschaften thermotroper Prototyp-Schichten erarbeitet und (5) theoretische Modellrechnungen zur Untersuchung des Einflusses der thermotropen Prototyp-Schichten auf die Effizienz eines Vollkunststoffkollektors durchgeführt.

Die Evaluierung unterschiedlicher thermotroper Schichten unter besonderer Berücksichtigung von Eigenschaftsanforderungen für die Kollektoranwendungen ergab, dass bislang entwickelte Systeme für den Einsatz in aktiv solar-thermischen Anlagen insbesondere hinsichtlich ihrer Schalttemperatur und Langzeitstabilität adaptiert und optimiert werden müssen. Unter den verschiedenen thermofunktionalen Materialien weisen vor allem thermotrope Systeme mit fixen Domänen (TSFD) das größte Entwicklungspotenzial für Überhitzungsschutzanwendungen in Sonnenkollektoren auf. In TSFD sind Streudomänen (so genannte thermotrope Additive), welche eine sprunghafte Änderung ihres Brechungsindex bei Erreichen eines Temperaturschwellwerts aufweisen, statisch in einem Matrixmaterial (im Allgemeinen ein Duromer) dispergiert.

Ein methodischer Ansatz zur Auswahl eines geeigneten Matrixmaterials für die Herstellung TSFD wurde erarbeitet, welcher die Erfassung von Vernetzungsparametern (Vernetzungsgeschwindigkeit, Vernetzungsgrad) und der Glasübergangstemperatur des Duromers einschließt. Am Beispiel eines UV vernetzenden Urethanacrylats wurde gezeigt, dass relevante Anwendungseigenschaften des Matrixmaterials mittels Dielektrischer Analyse (DEA), Infrarotspektroskopie im Modus der abgeschwächten Totalreflexion (ATR) und Dynamisch Mechanischer Analyse (DMA) umfassend charakterisiert werden können.

Für die umfassenden Untersuchungen an TSFD für Kollektoranwendungen wurden zahlreiche Prototyp-Schichten unter Variation des Matrixmaterials und des Additivtyps sowie dessen Konzentration hergestellt. TSFD Prototyp-Schichten wurden hinsichtlich ihrer solar-optischen Eigenschaften im ungeschalteten und geschalteten Zustand, ihrer Schalttemperatur und ihres Übergangstemperaturbereichs charakterisiert. Untersuchungen zu Unterschieden im Brechungsindex zwischen Matrix und Additiv, Additivgehalt und Streudomänengröße, -form und -verteilung wurden durchgeführt. Die detektierten morphologischen Parameter wurden den Überhitzungsschutzeigenschaften der Schichten gegenübergestellt. Zudem wurden Zusammenhänge zwischen den Eigenschaften der Einsatzstoffe und den Schalteigenschaften der thermotropen Schichten erarbeitet. Die Überhitzungsschutzeigenschaften der hergestellten

Schichten in einem Vollkunststoffflachkollektor mit Doppelstegplattenverglasung und schwarzem Absorber wurden über Modellrechnungen evaluiert.

Im ungeschalteten Zustand zeigten die TSFD Prototyp-Schichten eine hemisphärische solare Transmission zwischen 76 und 87%, wobei der Diffusanteil der transmittierten Solarstrahlung bei 14 bis 71% lag. Schalttemperaturen zwischen 40 und 80°C wurden ermittelt. Der Übergangstemperaturbereich variierte zwischen 10 und 25 K. Im geschalteten Zustand wurden hemisphärische solare Transmissionsgrade zwischen 62 und 85%, mit einem Diffusanteil zwischen 36 und 78% detektiert.

Unterschiede im Brechungsindex zwischen Matrix und Additiv, die 0.04 übersteigen erwiesen sich als vorteilhaft für die Überhitzungsschutzeigenschaften der Prototyp-Schichten. Der optimale Additivgehalt lag bei 5 m%. Die Rückstreueffizienz der TSFD wurde durch eine gleichmäßige Additivverteilung über die Schichtdicke begünstigt. Thermotrope Schichten, welche mit kurzkettigen Additiven formuliert waren, wiesen annähernd kugelförmige Streudomänen mit Durchmessern zwischen 0.5 und 3 µm auf. Derartige Materialien zeigten eine moderate Reduktion der hemisphärischen Transmission zusammen mit einem signifikanten Anstieg der diffusen Transmission oberhalb der Schalttemperatur. Langkettige Additive entwickelten anisotrope Streudomänen, die gekrümmte Plättchen bzw. Scheiben mit einem Durchmesser bis zu 50 µm und einer Dicke zwischen 100 und 400 nm darstellen. Derartige Streudomänen bewirkten deutlich verbesserte Überhitzungsschutzeigenschaften.

Die beste Rückstreueffizienz im Solarstrahlungsbereich wurde für TSFD Prototyp-Schichten festgestellt, deren Matrixmaterialien eine hohe Vernetzungsdichte und niedrige Kettensegmentbeweglichkeit (hohe Glasübergangstemperatur) aufwies. Thermotrope Materialien auf Basis weitmaschig vernetzter Matrixmaterialien zeigten den stärksten Anstieg der diffusen solaren Transmission oberhalb der Schalttemperatur. Für thermotropen Schichten auf Basis unpolarer Additive wurde eine Verbesserung der Überhitzungsschutzeigenschaften mit ansteigender Molmasse des Additivs beobachtet. Die Gegenüberstellung der thermischen Übergänge des Additivs und der Schaltcharakteristik der thermotropen Schichten ergab eine exzellente Korrelation. Dementsprechend können Schalttemperatur und

Schaltverhalten von TSFD durch die Auswahl geeigneter Additive maßgeschneidert werden.

Die Überprüfung des Einflusses der thermotropen Prototyp-Schichten auf die Effizienz eines Kunststoffkollektors ergab, dass verglichen zur Anbringung der Schichten am Absorber, deren Einsatz in der Verglasung den effizienten Arbeitstemperaturbereich des Kollektors erhöht und die Stagnationstemperaturen minimiert. Die thermotropen Schichten begrenzten die maximalen am Absorber auftretenden Temperaturen auf Werte zwischen 129 und 146°C. Absorbertemperaturen unter 130°C würden den Einsatz kostengünstiger Polymerwerkstoffe als Absorbermaterialien ermöglichen.

CONTENTS

1 Introduction and Scope

1.1 Motivation

The prospect of depletion and hence cost increases of conventional oil and gas occurrences and the adverse impacts of climate change and local air pollution as a result of fossil-fuel burning related emissions clearly reflect the risk of energy supply insecurity and the corresponding need for resource diversification (Vries et al., 2007; Sayigh, 1999). A substitution of fossil energy sources by renewable energy derived from direct or indirect solar resources thus contributes to both, the security of energy supply and protection of the environment (IPCC, 2007). In 2006 18% of the world primary energy demand was already provided by renewable energy. To enhance the deployment of renewable energy a range of policies and measures exist (IEA, 2004; IPCC, 2007). In the development of a sustainable energy system, the direct use of solar energy will significantly gain in importance. The proportion of solar radiation that reaches the earth's surface is more than 10,000 times the current annual global energy consumption (IPCC, 2007). In the heating sector, particularly in the demand for low temperature heats, there is the biggest potential for the substitution of fossil energy systems by solar energy. Low temperature heating, and to a lesser degree cooling, account for over 40% of the annual global consumer energy demand. In Europe, the final energy demand for heating (49% including low and high temperature heating) is even higher than for electricity (20%) or transport (31%) (EREC, 2006; Seyboth et al., 2008). The *European Solar Thermal Technology Platform (ESTTP)*, which was founded in 2005 and is expected to have a decisive influence on European research and development policies, prepared a solar thermal vision document stating: In 2030 solar thermal energy systems shall provide up to 50% of low temperature heating and cooling demand for the existing building stock. For new buildings, the vision is to establish the completely solar-heated building as a building standard by 2030 (Bokhoven et al., 2006; ESTTP, 2008).

For solar domestic hot water generation and space heating applications, glazed collectors are applied since several years, which absorb solar heat and pass it to a water storage tank using a heat carrier fluid (Goetzberger and Wittwer, 1993). In Europe, the second largest market for solar domestic hot water and space heating systems after China, mostly flat-plate solar collectors are used. In 2006, around 60.3 million m^2 (42.2 GW_{th}) of glazed flat-plate solar collector area was installed worldwide for hot water generation (Weiss, 2008). Worldwide installations are currently growing by ~20% per year. Concerning the cumulative installed capacity of glazed solar thermal collectors in 2007, Austria is ranked third in Europe (2.0 GW_{th}) after Germany (6.3 GW_{th}) and Greece 2.5 (GW_{th}). Austria's solar thermal capacity in operation per capita in 2007 (244 kW_{th}/1000 capita) is almost 8 times as high as the European average of 30.7 kW_{th}/1.000 capita (Hopwood, 2007; ESTIF, 2008; Faninger, 2008). To further strengthen the position of Austria in the solar thermal market, the *Austrian Solar Thermal Technology Platform (ASTTP)* was founded recently. The main aim of the ASTTP is to increase the Austrian research and development activities in the solar thermal sector by bringing together both, experts in solar technology and material scientists (Brunner et al., 2007; ASTTP, 2008). Domestic solar hot water systems are also expanding rapidly in developing countries (Weiss et al., 2008). However, the relatively high initial cost of solar collectors and systems discourages many people from investments (Raman et al., 2000).

Thus, to further increase market penetration of solar energy for domestic hot water generation and space heating, a reduction of the cost-benefit ratio is required (Koehl, 2006). Installation and hardware costs must, therefore, be reduced significantly. Conventional flat-plate collectors consist typically of a metallic absorber and a glass glazing. In most cases the absorber is mounted in an insulated aluminum box (Goetzberger and Wittwer, 1993). A potential method of reducing capital as well as installation costs of solar thermal systems is to replace conventional components by less expensive and light-weight plastics (Raman et al., 2000; Davidson et al., 2003; Kearny et al., 2005; Koehl, 2005; Wallner and Lang, 2006; Meir, 2008). The high potential for innovative advancements by the proper integration of polymeric materials in solar components and systems was already pointed out in several publications (Lang, 1995; Lang, 1999; Davidson et al., 2003; Raman et al., 2000; Meir, 2003; Rommel, 2003; Wallner and Lang, 2005; Wallner and Lang, 2006). A special issue of the journal *Solar Energy* (Volume 79, Issue 6 “Polymeric Materials for Solar Energy Applications”, edited by G.M. Wallner and R.W. Lang) as well as two *Leobener Symposia on Polymeric*

Solar Materials (in 2003 and 2008) organized by the Institute of Materials Science and Testing of Plastics at the University of Leoben and the Polymer Competence Center Leoben GmbH clearly reflect the interest in new, advanced materials for solar thermal applications. Currently also a task within the Solar Heating and Cooling Program (SHC) of the International Energy Agency (IEA) is dealing with ‘Polymeric Materials for Solar Thermal Applications’ (Task 39) (IEA SHC, 2008).

The advantages of polymers are obvious: Well established manufacturing processes could allow for cost-efficient large scale production and the preparation of even complex integrated structures in one step. The low weight of polymeric components would also decrease the cost of shipping, handling, and installation (Lang, 1995; Koehl, 2005; Wallner and Lang, 2005). In general, the price for plastics roughly correlates with their maximum service temperatures. Commodity plastics are relatively cost-efficient with market prices of about 2 €/kg. However, their long-term service temperature is limited to about 90°C. The costs for engineering plastics with long-term service temperatures up to 140°C range between 2 and 10 €/kg. For high-performance polymers with operating temperature ranges above 140°C expenses are exceeding 10 €/kg (Wallner and Lang, 2006).

The nominal operating temperature for solar domestic hot water and space heating systems is ~90°C. From this point of view cost-efficient commodity plastics are applicable for thermal collector systems. Nevertheless, conventional flat-plate collectors with selective absorbers reach stagnation temperatures up to 200°C (Khan and Brunger, 1995). These temperatures would cause deformation, ageing and degradation of absorbers produced from cost-efficient plastics. Thus, if the operating temperature range is ascertained not to exceed the maximum level of ~90°C, nearly any component of a collector system can potentially be realized by commodity plastics. If absorber temperatures are limited to 130°C the application of less expensive engineering plastics is possible. Hence, for potential applications of cost-efficient plastics in solar absorbers an appropriate design including overheating protection is essential. In other words, the key-challenge in the establishment of commodity polymeric materials in the solar thermal heating market is the implementation of an appropriate overheating protection. Hence, the main intention for the presented dissertation was to perform research on an overheating protection device for an all-polymeric solar collector.

1.2 Background

The absorber of conventional high performance flat-plate solar collectors reaches stagnation temperatures exceeding 200°C, e.g. during sunny periods of low hot water use, during daytime system maintenance or due to a pump or controller failure (Khan and Brunger, 1995). These temperatures exceed the maximum operating temperatures of cost-efficient polymeric absorbers with maximum service temperatures below 130°C. Absorbers made of such plastics tend towards irreversible deformation, degradation, and ageing when exposed to elevated temperatures above 150°C for prolonged periods. Thus, it is useful to consider methods to prevent the absorber from reaching the temperature at which mechanical and functional integrity is affected (Khan and Brunger, 1995; Kearney et al., 2005; Roberts et al., 2000). To date, no flat-plate solar collector with adequate overheating protection is available. However, in the literature two main methods are proposed to control the energy flux in flat-plate solar collectors, the one working via an increase in system losses, the other via a reduction in optical gain (Khan and Brunger, 1995; Roberts et al., 2000; Kearney et al., 2005; Resch et al., 2007; Wallner et al., 2008).

Concerning the increase in system losses a distinction is drawn between internal and external overheating protection mechanisms. The elimination of glazing gaps and the establishment of internal flow circuits are identified as potential internal methods of overheating protection. External overheating protection mechanisms include the activation of a radiator coupled to the absorber fluid, the use of a waste heat exchanger, or the application of a 3-phase heat-pipe system. The most prominent external system, however, is venting the collector to ambient air. Increasing the collector loss coefficient through external natural convection loops was modeled for a range of vent configurations in an all-polymeric flat-plate collector. It was found that venting limits stagnation temperatures to temperatures below 123°C. Venting combined with evaporative cooling from a wetted pad directly beneath the absorber plate lowered maximum absorber temperatures to values of 65°C (Roberts et al., 2000; Kearney et al., 2005).

Although an increase in system losses in general is a very reliable method to control stagnation temperatures, several disadvantages arise. Some implementations require complex installation, which can increase system complexity and can thus be a potential source of premature failure. Furthermore, systems with open loop are prone to clogging by leaves and insects (Roberts et al., 2000).

There are various possibilities to reduce the optical gain in a flat-plate solar collector. An example is the use of a clear absorber front with a reflective back and a heat absorbing fluid. Upon overheating the fluid drains out of the absorber and exposes the reflective back. Another approach is the reversible incorporation of insulative material between absorber and glazing. Although these methods are very efficient, they are complex to implement and require active control (Roberts et al., 2000).

As to the reduction in optical gain the application of thermotropic glazing is probably the most appropriate measure (Roberts et al., 2000). Thermotropic layers for overheating protection reversibly change their light transmittance from highly transparent to light diffusing upon exceeding a temperature threshold (e.g., Nitz and Hartwig, 2005; Seeboth, 2000). Overheating protection of solar collectors with thermotropic layers is well examined in the literature (Khan and Brunger, 1995; Wendker, 1998; Resch et al., 2007; Wallner et al., 2008). For the case of a conventional flat-plate collector with a selective absorber and a glass pane including a thermotropic layer the stagnation temperature were detected to be limited to 150°C and lower (Khan and Brunger, 1997). Thermotropic polymer blends applied for overheating protection purposes in a solar collector with metal absorber and transparent insulating glazing reduced maximum absorber temperatures to 115°C (Wendker, 1998). In a study performed within the framework of a research project funded by the State Government of Styria, Department *Zukunftsfonds Steiermark* (Graz, AT), and performed at the Polymer Competence Center Leoben GmbH (Leoben, A) in cooperation with the University of Leoben (Leoben, AT), the AEE-Institute for Sustainable Technologies (Gleisdorf, AT), and Dr. Schobermayr Kunststofftechnik (Ansfelden, AT), the potentiality of thermotropic layers to provide adequate overheating protection (i.e. maximum absorber temperatures of 80°C) in an all-polymeric flat-plate solar collector was evaluated (Resch et al., 2007;

Wallner et al. 2008). The impact of a thermotropic layer on overall collector efficiency was shown to be low as long as the solar transmittance exceeds 85% in the clear state. Stagnation temperatures of the solar collector can be reduced to temperatures between 80 and 90°C by using thermotropic layers in the glazing or on the absorber. Whereas for thermotropic layers in the glazing switching temperatures between 55 and 60°C are required, the solar transmittance should decrease between 75 and 80°C for thermotropic materials mounted on the absorber. To provide a limitation of the stagnation temperature to a maximum operating temperature of ~85°C a residual solar transmittance of 25% for a collector with twin-wall sheet glazing and black absorber is effectual. The development and design of thermotropic layers exhibiting a solar transmittance up to 60% in the opaque state would reduce absorber temperatures to values below 130°C.

Thermotropic layers are characterized by an automatic and quick activation, and are simple to implement. Special collector geometry modifications and further installations are not required (Roberts et al., 2000). Nevertheless, appropriate and cost-efficient material types fulfilling performance requirements for prolonged periods are not available so far.

1.3 Objectives and Scope

As mentioned above, within the research project funded by the State Government of Styria, Department *Zukunftsfonds Steiermark* (Graz, AT), and performed at the Polymer Competence Center Leoben GmbH (Leoben, AT) in cooperation with the University of Leoben (Leoben, AT), the AEE-Institute for Sustainable Technologies (Gleisdorf, AT), and Dr. Schobermayr Kunststofftechnik (Altenfelden, AT), it was shown by theoretical modeling that thermotropic layers can provide adequate overheating protection for an all-polymeric solar collector (Resch et al., 2007; Wallner et al., 2008). In the past thermotropic systems have been developed and investigated mainly for active daylight control in transparent facades (e.g. Nitz and Hartwig, 2005; Seeboth et al., 2000). In contrast, thermotropic layers for overheating protection purposes in solar collectors were not designed and characterized systematically so far. Thus the overall aim of this dissertation is to provide fundamental knowledge and scientific basis for the development of polymeric thermotropic materials with overheating protection properties that are in accordance with performance requirements deduced from theoretical modeling of an all-polymeric solar collector. Specifically, the following objectives were defined:

(1) Evaluation and strength-weakness analysis of existing thermotropic layers produced from polymeric materials concerning their applicability in solar collectors.

(2) Polymer physics based development and design of thermotropic prototype-layers for solar collector applications.

(3) Comprehensive characterization of thermotropic prototype-layers as to relevant morphological parameters and performance properties.

(4) Establishment of structure-property relationships between the performance properties and the inner material structure and formulation parameters of thermotropic prototype-layers, which shall provide a basis for further research work and a systematic material optimization.

(5) Investigations and model calculations concerning the effect of thermotropic prototype-layers on the efficiency of an all-polymeric flat-plate collector.

1.4 Structure of the Thesis

According to the above objectives, this dissertation presents a series of papers on the development and evaluation of thermotropic materials for overheating protection of solar collectors. The dissertation is structured corresponding to the process of material design, characterization and optimization, and contains 6 chapters:

Chapter 1: Introduction and Scope

Chapter 2: Overheating Protection with Thermotropic Materials – State of Technology

Chapter 3: Investigation of Matrix Materials for Thermotropic Systems with Fixed Domains

Chapter 4: Performance Properties of Thermotropic Polymer Systems with Fixed Domains

Chapter 5: Structure-Property Correlations of Thermotropic Polymer Systems with Fixed Domains for Solar Collector Applications

Chapter 6: Conclusions and Future Work

Following the introduction, in Chapter 2 thermotropic polymers developed so far for overheating protection purposes are surveyed and discussed. Basic performance properties are defined, which are relevant for the applicability of thermotropic materials to prevent overheating in solar collectors. Existing thermotropic materials are reviewed with respect to their capability to fulfill these requirements and appropriate material types are identified.

Based on the material selection of Chapter 2 and considering the performance requirements established, in Chapters 3 to 5 the preparation and characterization of polymeric thermotropic systems with fixed domains (TSFD) for solar collector applications is discussed. Starting with a treatment of the raw materials, Chapter 3 describes a polymer physics based approach for the selection of a matrix material appropriate to the production of TSFD. Chapter 4 deals with a comprehensive characterization of TSFD concerning relevant performance parameters, such as switching temperature, transition gradient and reduction of solar transmittance. These material characteristics are related to morphological properties, like the nature of the material constituents and scattering domain size and distribution. In Chapter 5 the relationships between formulation parameters, inner material structure and the light-shielding properties of TSFD are established. Furthermore the effect of the produced thermotropic prototype-layers on the collector efficiency and on maximum absorber temperature is investigated applying theoretical modeling of an all-polymeric flat-plate collector with twin-wall sheet glazing and black absorber.

In Chapters 2 to 5 a short introduction to the respective topic is followed by relevant papers published by the main author of this dissertation along with co-authors. The introduction surveys the state of the art as well as specific scientific problems and requirements and outlines the main content of the papers. The subsequent scientific publications include the detailed experimental background along with the data reduction and the results of the research work.

In Chapter 6 the outcome and contributions of the dissertation are reviewed. Essential conclusions concerning the development of thermotropic materials to prevent overheating in solar collectors are summarized. The subsequent outlook points out open issues and suggests approaches for their solution and future work.

1.5 Key Literature

ASTTP (2008). Austrian Solar Thermal Technology Platform <www.asttp.at>, website accessed October 2008.

Brunner, C., Fechner, H., Fink, C., Gottwald, D., Guggenberger, W., Hochreiter, E., Holter, C., Huemer, H., Jaehnig, D., Lang, R.W., Podesser, E., Rabensteiner, G., Schnitzer, H., Slawitsch, B., Streicher, W., Steinmauer, G., Wallner, G.M., Weiss, W. (2007). Positionspapier fuer ein oesterreichisches Solarforschungs- und Technologieprogramm, download from <www.asttp.at>.

Bokhoven, T., Cotton, N., Drueck, H., Pilgaard, O., Stryi-Hipp, G., Weiss, W., Wittwer, V. (2006). Solar Thermal Vision 2030 – First version of the vision document for the start of the European Solar Thermal Technology Platform (ESTTP), download from <www.esttp.org>.

Davidson, J.H., Mantell, S.C., Jorgensen, G.J. (2003). Advances in Solar Energy **15**, 149.

ESTIF (2008). Solar Thermal Markets in Europe – Trends and Market Statistics 2007, download from the website of the European Solar Thermal Industry Federation (ESTIF) <www.estif.org>.

ESTTP (2008). European Solar Thermal Technology Platform <www.esttp.org>, website accessed October 2008.

EREC (2008). European Renewable Energy Council <www.erec-renewables.org>, website accessed October 2008.

Faninger (2008). Der Solarmarkt in Österreich 2006, Erhebung fuer Internationale Energie Agentur im Auftrag des Bundeministeriums fuer Verkehr, Innovation und Technologie BMVIT, download from <www.uni-klu.ac.at>.

Goetzberger, A., Wittwer, V. (1993). Sonnenenergie – Thermische Nutzung, Teubner, Stuttgart.

Hopwood, D. (2007). Renewable Energy Focus **July/August**, 46.

IEA (2004). Policies of IEA countries - 2004 review, download from the website of the Organization for Economic Cooperation and Development (OECD) <www.oecd.org>.

IEA SHC (2008). Polymeric materials for solar thermal applications <www.iea-shc.org/task39/>, website accessed October 2008.

IPCC (2007). Climate Change Fourth Assessment Report – Mitigation, Chapter 4: Energy Supply, download from the website of the Intergovernmental Panel on Climate Change (IPCC) <www.ipcc.ch>.

Kearney, M., Davidson, J., Mantell, S. (2005). Journal of Solar Energy Engineering **127**, 421.

Khan, A., Brunger, A. (1997). In Proc. 23rd Annual Conference of the Solar Energy Society of Canada Inc: Implementing Sustainable Energy in a Changing World, pp. 119-124, June 5-7, Vancouver, CA.

Koehl, M. (2005). Concept Paper for a Task of the Solar Heating and Cooling Programme of the International Energy Agency 'Polymeric Solar Materials'.

Lang, R.W. (1995). Das Bauzentrum **9**, 95.

Lang, R.W. (1999). Chemie **October 1999**, 15.

Lang, R.W., Wallner, G.M. (2005). Solar Energy **79**, 571.

Meir, M., Rekstad, J., (2003). In Proc. 1st Leobener Symposium Polymeric Solar Materials (*G. M. Wallner and R.W. Lang*, Eds.), pp. II–1-8, November 6-7, Leoben, AT.

Meir, M. (2008). In Proc. 2nd Leobner Symposium Polymeric Solar Materials (*G. M. Wallner and R.W. Lang*, Eds.), pp. I–1-6, February 7-8, Leoben, AT.

Nitz, P., Hartwig, H. (2005). Solar Energy **79**, 573.

Raman, R., Mantell, S., Davidson, J., Wu, C., Jorgensen, G. (2000). Journal of Solar Energy Engineering **122**, 92.

REN21 (2008). Renewables 2007 Global Status Report, download from the website of the Renewable Energy Policy Network for the 21st Century (REN21) <www.ren21.net>.

Roberts, J.P., Brandemuehl, M.J., Burch, J.D, Gawlik, K.M. (2000). In Proc. Solar 2000, American Solar Energy Society Annual Conference, pp. 273-278, June 16-21, Madison, US.

Rommel, M., (2003). In Proc. 1st Leobener Symposium Polymeric Solar Materials (*G. M. Wallner and R.W. Lang*, Eds.), pp. XXI–23-24, November 6-7, Leoben, AT.

Sayigh, A. (1999). Applied Energy **64**, 15.

Seeboth, A., Schneider, J., Patzak, A. (2000). Solar Energy Materials and Solar Cells **60**, 263.

Seyboth, K., Beurskens, L., Langniss, O., Sims, R.E.H. (2008). Energy Policy **36**, 2460.

Vries, B.J.M., van Vuuren, D.P., Hoogwijk, M.M. (2007). Energy Policy **35**, 2590.

Wallner, G.M., Lang, R.W. (2006). Erneuerbare Energie **2-06**, 10.

Weiss, W., Bergmann, I., Faninger, G. (2008). Solar heat worldwide: Markets and contribution to the energy supply Edition 2008, download from the website of the Solar Heating and Cooling Program of the International Energy Agency <www.iea-shc.org>.

2 Overheating Protection with Thermotropic Materials – State of Technology

2.1 Introduction

Thermotropic layers are inherently switching, which permits the light and energy flux to be adapted to an external temperature stimulus. For overheating protection purposes a reversible transition from highly transparent to light diffusing upon reaching a certain threshold temperature is required. The autonomous shading of the thermotropic layer is induced by light scattering from mesoscopic particles which exhibit an index of refraction that is different to that of the surrounding medium above the defined transition temperature. Three main types of thermotropic layers based on various polymers were established in the past. These systems differ in their switching mechanisms. Whereas in thermotropic hydrogels and thermotropic polymer blends the formation of scattering particles is based on a phase separation, in thermotropic systems with fixed domains, the scattering domains are embedded statically in a matrix material (e.g. Wilson, 2000; Seeboth et al., 2000; Nitz and Hartwig, 2005).

Aside from recent publications associated with the present project (Resch et al., 2007; Wallner et al., 2008), the suitability of thermotropic layers to prevent overheating in solar collectors was proved in former studies by Khan and Brunger (1995) and Wendker (1998). However, research on thermotropic systems for overheating protection purposes so far focused on the development of ‘smart windows’ for light-shielding applications in transparent facades (e.g. Nitz and Hartwig, 2005; Seeboth et al., 2000; Raicu et al., 2002; Georg et al., 1998; Beck et al., 1995; Wilson, 1994; Watanabe, 1998). Compared to glazing applications, thermotropic materials applied to control stagnation temperatures in solar collectors are exposed to harsher environmental conditions and require different performance properties. Among these especially higher switching temperatures and appropriate long-term stability at elevated temperatures are the most important (Wendker, 1998; Resch et al., 2007; Wallner et al., 2008).

Research and development on thermotropic materials for overheating protection in solar collectors initially requires detailed knowledge on

- necessary performance properties,
- existing material types and their functional principle,
- advantages and disadvantages of material types developed so far, and
- the potential to adapt and modify existing material types.

Information as to these issues allows for an appropriate material selection, especially from a polymer engineering and science point of view, which provides the basis for further developments and systematic optimization. However, a comprehensive survey on thermotropic materials for overheating protection purposes along with relevant material characteristics was not reported yet. Hence, this chapter is concerned with the detailed evaluation of thermo-functional material types developed so far. Specific focus is directed towards their applicability and adaptability for active solar thermal systems.

2.2 Paper 1

Paper 1: Thermotropic layers for flat-plate collectors – A review of various concepts for overheating protection with polymeric materials
by K. Resch and G.M. Wallner
(to be published in: *Solar Energy Materials and Solar Cells*)

This paper includes an overview of the developments on thermotropic hydrogels, thermotropic polymer blends and thermotropic systems with fixed domains for overheating protection purposes. Relevant performance properties to provide adequate overheating protection for solar thermal collectors are defined. Existing material formulations are evaluated with respect to their ability to meet these requirements.

2.3 Key Literature

Beck, A., Koerner, W., Scheller, H., Fricke, J., Platzer, W.J., Wittwer, V. (1995). Solar Energy Materials & Solar Cells **36**, 339.

Georg, A., Graf, W., Schweiger, D., Wittwer, V., Nitz, P., Wilson, H.R. (1998). Solar Energy **62**, 215.

Khan, A., Brunger, A. (1997). In Proc. 23rd Annual Conference of the Solar Energy Society of Canada Inc: Implementing Sustainable Energy in a Changing World, pp. 119-124, June 5-7, Vancouver, CA.

Nitz, P., Hartwig, H. (2005). Solar Energy **79**, 573.

Raicu, A., Wilson, H.R., Nitz, P., Platzer, W., Wittwer, V., Jahns, E. (2002). Solar Energy **72**, 31.

Resch, K., Hausner, R., Wallner, G.M. (2007). In Proc. Solar World Congress 2007, pp. 561-565, September 18-21, Beijing, CN.

Seeboth, A., Schneider, J., Patzak, A. (2000). Solar Energy Materials and Solar Cells **60**, 263.

Wallner, G.M., Resch, K., Hausner, R. (2008). Solar Energy Materials and Solar Cells **92**, 614.

Watanabe, H. (1998). Solar Energy Materials & Solar Cells **54**, 203.

Wendker, K. (1998). „Untersuchungen zum Einsatz thermotroper Schichten in Sonnenkollektoren“, Diploma Thesis, Fraunhofer Institute for Solar Energy Systems, Freiburg, DE.

Wilson, H. R. (1994). SPIE; Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XIII **2255**, 214.

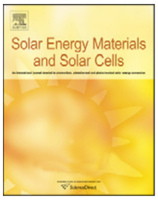
Wilson, H.R. (2000). Functional Materials – EUROMAT 99 **13**, 221.

Solar Energy Materials & Solar Cells ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Review

Thermotropic layers for flat-plate collectors—A review of various concepts for overheating protection with polymeric materials

Katharina Resch [a,*], Gernot M. Wallner [b]

[a] Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria
[b] Institute of Materials Science and Testing of Plastics, University of Leoben, Franz-Josef Strasse 18, 8700 Leoben, Austria

ARTICLE INFO

Article history:
Received 15 April 2008
Accepted 9 September 2008

Keywords:
Solar collectors
Overheating protection
Thermotropic hydrogels
Thermotropic polymer blends
Thermotropic systems with fixed domains

ABSTRACT

Within this paper a comprehensive review of the developments of thermotropic hydrogels, thermotropic polymer blends and thermotropic systems with fixed domains for overheating protection purposes is given. In addition, performance properties for thermotropic layers to prevent overheating in solar collectors are defined. The different thermotropic material classes are discussed as to their ability to meet these requirements. The review shows that thermotropic layers developed so far need to be adapted as to switching temperature and long-term stability for applicability in solar thermal collectors.

Contents

1. Introduction

Thermotropic glazings are inherently switching layers which permit the light and energy flux to be adapted dynamically to climatic demands [1–3]. Materials which change their light transmission behavior reversibly from highly transparent to light diffusing upon reaching a certain threshold temperature can provide overheating protection for active and passive solar thermal systems [1,3–8]. Polymeric materials are playing a key role in thermotropic solar control layers [5]. In the past thermotropic systems for active daylight control in transparent facades have been developed and investigated mainly [1–3,9–25]. Some recent publications deal with the characterization of thermotropic materials for all-polymeric solar collectors [26,27]. Nevertheless, the developments on thermotropic materials for overheating protection purposes are not reviewed extensively in the literature. Thus the overall objective of the present paper is to give a comprehensive review of thermotropic systems. Specific focus is directed towards the definition of basic demands placed on thermotropic materials for active solar energy related applications and the potential of existing material formulations to meet these requirements.

---

[*] Corresponding author.
E-mail address: resch@pccl.at (K. Resch).

0927-0248/$ - see front matter
doi:10.1016/j.solmat.2008.09.004

2. Thermotropic systems

In general, the autonomous shading of the thermotropic layer is induced by light scattering from particles with dimensions comparable to the wavelength of the solar spectral range which exhibit an index of refraction that is different to that of the matrix above the defined transition temperature [3,5]. On one hand thermotropic behavior may be achieved by an alteration in the structure of the liquid crystalline phase with an anisotropic index of refraction from optically anisotropic to isotropic at a corresponding temperature as in the case of liquid crystal systems [2,3,18]. Liquid crystal systems are not considered within this paper. On the other hand scattering can be induced by the formation of local differences in the refractive index by phase separation or a change in refractive index of one or more components [2,3,5]. This is the case in thermotropic hydrogels, thermotropic polymer blends and thermotropic systems with fixed domains. The following discussion merely focuses on these thermotropic systems.

2.1. Thermotropic hydrogels

Thermotropic hydrogels are chemically or physically cross-linked polymer networks which are poured with appropriate water (or solvent) content. At low temperatures the aqueous solution is dissolved homogeneously on the molecular level, so that a clear state is achieved. Above the switching temperature scattering domains are formed by an aggregation of the polymers and/or by separation of free water (or solvent) from the polymer network (e.g. [2,3,5,10–12,16,20]) and the layer becomes light diffusing.

A multiplicity of thermofunctional substances exhibiting a cloud point have been developed mostly for biomedical applications, such as carriers for controlled drug release and drug targeting, biotechnology and tissue engineering (e.g. [28–30]). Thermotropic hydrogels have also received attention for applications in architecture as light-shielding glass [2,3,15].

As functional components and/or base materials of thermotropic hydrogels developed so far various polymer types were used. A classification as to main polymer component is given in Table 1. Though, not all material modifications and variations are surveyed within the scope of the present paper. A review on thermo-responsive hydrogels for pharmaceutical applications and drug delivery is given in Peppas et al. [28] and Schmaljohann [29], respectively. The synthesis of thermosensitive water-soluble copolymers is reviewed and discussed in Dimitrov et al. [31]. The following discussion goes into details concerning compositions and properties merely for thermotropic hydrogels produced for light-shielding applications.

Comprehensive research and development was done on thermotropic hydrogels based on polyvinylpolymers. For instance Kühl [32], Falicoff et al. [33], Chahroudi [34–36], Starovoytova and Spevacek [37], Nies et al. [38], Loozen et al. [39] and Guo et al. [40] investigated thermofunctional aqueous solutions of polyvinylmethylether. Chahroudi [41], Kröner et al. [42], Arndt et al. [30], Moerkerke et al. [43] and Reyntjens et al. [44] discussed gels produced by cross-linking or copolymerizing. Kühl [32] prepared the first thermotropic hydrogel by mixing polyvinylmethylether, agar-agar and water and laminated the functional material between glass panes. In 1995 Chahroudi [41] presented Cloud Gel^{TM} for light-shielding applications (Suntek Inc., Albuquerque, USA), based on an aqueous polyvinylmethylether solution which was made capable of UV curing. Measurements on a 1 mm thick

Table 1
Survey on thermotropic hydrogels (this list is not exhaustive)

Classification	Polymer class	Polymer type	Author
Synthetic polymers	Polyvinyl polymers	Polyvinylmethylether	Arndt et al. [30], Kühl [32], Falicoff [33], Chahroudi [34–36], Starovoytova and Spevacek [37], Nies et al. [38], Lozen et al. [39], Guo et al. [40], Chahroudi [41], Kröner et al. [42], Moerkeke et al. [43], Reyntjens et al. [44]
		Polyvinylalcohol	Chahroudi [34–36], Kühl [45,46], Nonaka et al. [47], Aoshima [48], Wu et al. [49], Mitsumata [50], Byun et al. [51], Boyko et al. [52], Kim et al. [53], Zhang et al. [54], Oktar et al. [55]
	Polymers with amide groups	*N*-isopropylacrylamide	Chahroudi [41], Kim et al. [53], Zhang et al. [54], Oktar et al. [55], Nishimura et al. [56], Chytry et al. [57], Neradovic et al. [58], Zhu et al. [59], Liu et al. [60,61], Park et al. [62], Geever et al. [63], Zhu et al. [64], Ju et al. [65], Kim et al. [66]
		N,*N*-dimethylacrylamide	Mueller [67,68]
		Vinylcaprolactames	Kröner et al. [42], Kühl [69], Eisele and Burchard [70], Makhaeva et al. [71], Meeussen et al. [72], Verbrugghe et al. [73], Gao et al. [74], Vihola et al. [75]
		N-vinyl-5-methyl-2-oxazolidinone	Walles and Tousignat [78], Walles [79]
		Poly-2-isopropyl-2-oxazoline	Uyama and Kobayashi [80]
		Polymethyl-2-acetamidoacrylate	Okamura et al. [81–83], Mori et al. [84,85], Lee and Bucknall [86]
		Polyvinylalkylamides	Suwa et al. [87,88], Kishida et al.[89], Yamamoto et al. [90,91]
	Various polyethers	Hydrogel of lactitol based polyether polyol	Lin et al. [92]
		Hydrogel of polyglycidols	Dworak et al. [93], Jamroz-Piezga et al. [94]
		Aqueous solutions of ethyleneoxide/propyleneoxide	Nishimura et al. [56], Bösing et al. [95], Campese et al. [96], Song et al. [97], Mori et al. [98]
		Hydrogel of polyether compound with ethyleneoxide groups	Meinhardt [99]
	Others	Aqueous acrylourethane resins	Howard and Nulph [100], Zalucha [101]
		Hydrogel of polyacrylicacid	Kühl [102], Tanaka [103]
		Solution of metal sulphate salt in water	Stephens [53]
Biopolymers	Cellulose derivatives	Hydrogels of hydroxypropylcellulose	Watanabe [105]
			Schneider and Seeboth [18], Seeboth et al. [18,21]
		Hydrogels of cellulose esters	Zhou et al. [106]

Cloud Gel^{TM} laminated between polymer films showed that the solar transmittance decreases from 82% in the clear state to 5% in the opaque state at switching temperatures variable between 10 and 70 °C [4,16].

Kuehl [45,46], Chahroudi [34–36], Nonaka et al. [47], Aoshima et al. [48], Wu et al. [49] and Mitsumata et al. [50] described thermofunctional gels which were produced from aqueous solutions of polyvinylalcohol, its copolymers or terpolymers and modifications. In many cases polyvinylalcohol was also incorporated into cross-linked polymers (e.g. polyacrylicacid [51], poly(*N*-vinylcaprolactam) [52] or poly(*N*-isopropylacrylamide) [53–55]) for the production of hydrogels with semi-interpenetrating networks.

Polymers containing amide groups were constituents of numerous developments concerning thermotropic hydrogels. Poly-*N*-isopropylacrylamide and its copolymers were frequently cited as polymer base for the production of thermotropic hydrogels, for example by Chahroudi [41], Nishimura et al. [56], Chytry et al. [57], Neradovic et al. [58], Zhu et al. [59], Liu et al. [60,61], Park et al. [62], Geever et al. [63] and Zhang et al. [64]. Furthermore also semi-interpenetrating networks of *N*-isopropylacrylamide with alginate [65] and polyethyleneoxide [66] were developed. Mueller [67,68] depicted the production of thermotropic hydrogels with a lower critical solution temperature from copolymers of *N*,*N*-dimethylacrylamide and hydrocarbon-acrylate, which are partly crosslinkable by energetic radiation. Polyvinyllactams were also considered as polymer base for the production of thermotropic hydrogels. In Kröner et al. [42], Kühl [69], Eisele and Burchard [70], Makhaeva et al. [71] and Meeussen et al. [72] aqueous solutions of different vinylcaprolactames were described. *N*-vinylcaprolactames-graft-polyethyleneoxide was produced by Verbrugghe et al. [73]. Thermally responsive microgel particles composed of *N*-vinylcaprolactames are reported by Gao et al. [74] and Vihola et al. [75]. Rullier [76,77] developed a functional gel filling for a double glazing, which was produced from different acrylamides, water and derivatives from polyvinylalcohol and poylvinylcaprolactam. Walles and Tousignat [78] and Walles [79] prepared thermotropic hydrogels by mixing homopolymers or copolymers of *N*-vinyl-5-methyl-2-oxazolidinone, water and glycerol to depress the freezing point. Uyama and Kobayashi [80] reported on thermotropic hydrogels produced from poly-2-isopropyl-2-oxazoline. Thermotropic hydrogels based on poly-methyl-2-acetamidoacrylate, its modifications and copolymers were discussed for instance in Okamura et al. [81–83], Mori et al. [84,85] and Lee and Bucknall [86]. Suwa et al. [87,88], Kishida et al. [89] and Yamamoto et al. [90,91], described thermosensitive hydrogels based on poly-*N*-vinylalkylamides and its modifications.

Also aqueous solutions of some polyethers exhibit a cloud point temperature. Examples are given in Lin et al. [92], Dworak et al. [93] and Jamroz-Piegza et al. [94]. The reversible solubility of ethyleneoxide or propyleneoxide and their copolymers in water or other solvents was utilized by Nishimura et al. [56], Bösing et al. [95], Campese et al. [96], Song et al. [97] and Mori et al. [98] for the production of functional layers. Meinhardt [99] produced thermotropic hydrogel called TALD (*t*emperatur*a*bhängige *L*icht*d*urchlaessigkeit) based on a polyether compound with ethyleneoxide groups, a base, a carboxyvinyl polymer and water. The application of a non-ionic wetting agent enhanced reversibility and allowed for the control of the phase transition temperature. The addition of glycol improved the frost resistance. For a 1 mm thick TALD-hydrogel laminated between glass panes a solar transmittance of 84% and 47% in clear and opaque state is reported, respectively, at switching temperatures adjustable between 5 and 60 °C [4]. Howard and Nulph [100] and Zalucha et al. [101] generated thermotropic films by blending water and optionally ethylenic monomers into different acrylourethane resins.

Kühl [102] and Tanaka et al. [103] introduced formulations based on esters of polyacrylacid. A different approach is a metal sulphate salt solution presented by Stephens [104], which exhibits a decreasing salt solubility with increasing temperature.

Recent attempts were considering biologically degradable polymers, such as cellulose derivatives for the production of thermotropic hydrogels. Watanabe [105] developed a thermotropic hydrogel with enhanced long-term stability consisting of water, hydroxypropylcellulose (HPC), 5% sodium chloride aqueous solution and an amphipathic substance acting as a spacer, which prevents a complete phase separation [1,3,5,54]. The *Affinity Intelligent Window*^{TM} of sizes up to 1 m^2 was produced by laminating the hydrogel between glass panes. If insulating glazing units were used for lamination the solar transmittance changed from 44% in the clear state to 9% in the opaque state [23]. Switching temperatures between 25 and 60 °C were realized [15]. Schneider and Seeboth [18] and Seeboth et al. [21,25] reported on thermotropic hydrogels based on HPC, natriumchloride and either hydroxyethylcellulose (HEC) or gellan gum, instead of an amphipathic substance to avoid ageing. The different materials changed their light transmittance at temperatures between 20 and 40 °C from 80–98% in clear state to $<5\%$ in opaque state for a wavelength of 600 nm [18,21]. Thermosensitive hydrogels prepared from cellulose ester derivatives are described in Zhou et al. [106] which show precipitation temperatures between 54 and 96 °C.

2.2. Thermotropic polymer blends

In general, polymers are incompatible with one another as a result of low entropy of mixing and the positive energy of mixing between polymers. Exceptions to this rule are for example metastable, partly miscible systems which exhibit a lower critical solution temperature (LCST). At low temperatures the polymers interact via salt formation, hydrogen bonding, complex formation, π-electron interaction or dipolar interaction. The miscibility decreases with increasing temperature associated with the formation of domains [2,5,19,20,22,107]. Thus the material undergoes a transition from clear to cloudy. An overview of thermotropic polymer blends developed so far for light-shading purposes is given in Table 2.

The specific utilization of this phase-separation mechanism for thermotropic polymer blends was first described by Siol et al. [107], who manufactured thermotropic layers showing clear/cloudy transitions from various acrylate based polymers and chlorinated rubber or polystyrene. The transition temperature was varied between 60 and 140 °C by a modification in the proportions of the interacting groups, by a change in the proportions of the polymers, by the addition of one or more low molecular weight substances or by a variation of the molecular weight of the polymers. Eck [19] and Eck et al. [108] developed thermotropic polymer blends based on interpenetrating networks by thermally crosslinking styrene-hydroxyethylmethacrylate random copolymers using a trifunctional isocyanate with polypropyleneoxide being simultaneously grafted onto the network. The breadth of the temperature range, in which turbidity occurs, could be adjusted from 30 to 100 °C by the cross-link density. The solar transmittance changed from 89% in clear state to 37% in opaque state. In Jahns et al. [109] switching temperatures between 40 and 130 °C were achieved with a dissolution of styrene-hydroxyethylmethacrylate random copolymers and polypropyleneoxide that was radiation cured during or after evaporation of the solvent. The material exhibited solar transmittance values of 87% and 38% in

Table 2
Compositions of thermotropic polymer blends

Classification	Polymer 1	Polymer 2	Author
Acrylate based	Polymethylmethacrylate	Chlorinated rubber	Siol et al. [107]
	Methylmethacrylate-butylmethacrylate copolymer		
	Polyisobutylmethacrylate		
	Poly-2-ethylhexylmethacrylate		
	Isobutylmethacrylate and 2-ethylhexylmethacrylate		
	Ethylacrylate	Polystyrene	
Styrene based	Styrene-hydroxyethylmethacrylate random copolymers	Polypropyleneoxide	Eck [19], Eck et al. [108]
	Styrene-hydroxyethylmethacrylate random copolymers	Polypropyleneoxide	Jahns et al. [109]
	Dissolution of styrene, hydroxyethylmethacrylate and allylmethacrylate	Polypropyleneoxide butylenoxide copolymer	Jahns et al. [110]

Table 3
Compositions of thermotropic systems with fixed domains

Classification	Matrix material(s)	Thermotropic component(s)	Author
Matrix not cross-linked			
Amorphous thermoplastics	Thermoplastic copolyesters	Octadecane	Dabisch [112]
	Polymethylmethacrylate	Eicosane[a]	
	Thermoplastic polystyrene	Ester types	
Semi-crystalline Thermoplastics	Thermoplastic polyamide	Ester types	
		Random copolymer of ethylene and glycidyl	Buehler and Hewel [113]
		Methacrylate-butadiene-styrene core-shell block-copolymer	
Matrix cross-linked			
Silicon resin	Silicon resin	Ester types[a]	Dabisch [112]
		Waxy polymer $(C_2F_3Cl)_x$	Charoudi [34]
Thermoset resins	Polyesters resins based on aromatic or aliphatic carboxylic acid and aliphatic diols, solvent trichloroethylene	Ester types	Dabisch [112]
	Resin based on phtalic anhydride, soy oil, pentaerythrit and solvent	n-Octadecane, eicosane	Meinhardt et al. [114]
Peroxidic curable resins	Epoxy resin, crosslinker: dibenzoylperoxide, cyclohexanonperoxide, aminfunctionalized crosslinker, isocyanatic crosslinker	n-Eicosane, n-octadecane	Bicer et al. [115]
UV curing resins	Polyesteracrylate, methacrylicacid-methylester, UV initiator	n-Octadecane	Bicer et al. [116]
	Polyesteracrylate, divinylbenzol, UV initiator	n-Eicosane	
	Polyesteracrylate, epoxyacrylate, acrylicacid, tetrahydrofurfurylacrylate, UV-initiator	n-Octadecane	Schwitalla et al. [117]
	Photo-crosslinkable matrix solutions	n.a.	Resch et al. [26,27]

n.a. data not available.

[a] System with switching direction from opaque to transparent.

clear and scattering state, respectively. Kleinke et al. [110] suggested a transparent sheath layer which surrounds the thermotropic core material to provide stickiness control and mechanical strength and makes it possible to put the material into film form. To enhance coextrusion with sheath layers Jahns et al. [111] produced polymer blends based on a dissolution of styrene, hydroxyethylmethacrylate and allylmethacrylate, which are mixed homogeneously with a polypropyleneoxide-butyleneoxide copolymer. After outgassing in an extruder and granulating the granulate material was processed into films with a switching temperature of 30 °C by blow-molding.

2.3. *Thermotropic systems with fixed domains*

In thermotropic systems with fixed domains (TSFD) scattering particles, which exhibit a sudden change of refractive index with temperature, are statically embedded in a matrix material. At low temperatures the layer is translucent, as the refractive indices of matrix and domain are almost equal. The differing temperature dependence of the refractive index for the components above the switching threshold causes the thermotropic film to turn opaque. Vice versa if the refractive index of matrix and domain are differing at low temperatures and are almost equal above the switching temperature the thermotropic system exhibits a transition from an opaque to a transparent state. However, such systems are not appropriate for overheating protection purposes. Whereas in some developments thermoplastics were considered as matrix materials for TSFD, other attempts focused on the embedding of scattering domains in cross-linked polymers [26,27,34,112–117]. A summary of different systems is presented in Table 3.

The combination of a monomer compound and a polymer matrix for TSFD was proposed by Dabisch [112], who prepared numerous thermotropic materials with switching temperatures between 5 and 40 °C based on both thermoplastic and duromer matrix materials and different ester types and alcanes as thermotropic components. Both thermotropic layers switching from a transparent to an opaque state and from a scattering to a clear state were prepared. Chahroudi [34] suggested the embedding of a waxy polymer in silicon rubber. Buehler and Hewel [113] described TSFD composed of a thermoplastic polyamide matrix and impact-modifier copolymers as thermotropic components, which is commercially available and can be converted in any shape by injection-molding or extrusion. In Meinhardt et al. [114] a dissolution of alcanes in a resin based on pthalic anhydride, soy oil, pentaerythrit and a solvent was converted into a functional film. In a further development Bicer et al. [115] suggested the use of modified epoxy resins, which are peroxidic curable, as matrix material. For ecologic and economic reasons Bicer et al. [116] prepared thermotropic casting resin systems by dissolving the monomer compound in a matrix solution, which contains photo-hardening oligomers, reactive thinners as well as photo-initiators and can be cured using photo-radiation. In a further modification of this composition Schwitalla et al. [117] added a thixotrope component to enhance retrofitting of existing glazing. For these functional films [114–117] switching temperatures between 20 and 35 °C and moderate switching ranges of 25% were achieved [23,114–117]. Resch et al. [26,27] discussed TSFD for solar thermal applications based on UV curable acrylate oligomers and non-polar as well as polar additives, which show moderate clear/cloudy transitions (9%) in the temperature range between 40 and 75 °C.

3. Strengths and weaknesses

In the following basic requirements for thermotropic materials to provide adequate overheating protection for solar thermal collectors are described. Subsequently the potentialities of thermotropic hydrogels, polymer blends and systems with fixed domains to meet these specifications are discussed. A summary and comparison of their performance properties is given in Table 4.

In Seeboth et al. [2] and Watanabe [15] a set of requirements is defined, whereof thermotropic materials should fulfill most for industrial applications. Some further specifications arise, when thermotropic layers are applied to prevent overheating of solar thermal systems [8,9,118]. Theoretical modeling of an all-polymeric flat-plate collector with twin-wall sheet gazing and black absorber shows that for adequate overheating protection (i.e. stagnation temperatures ranging from 80 to 140 °C) switching temperatures between 55 and 60 °C and 75 and 80 °C for thermotropic glazing and thermotropic absorbers, respectively, as well as a residual hemispheric solar transmittance below 60% in the opaque state are effectual [8,9]. The influence of the thermotropic layer on the overall collector efficiency is insignificant as long as the solar transmittance is higher than 85% in the clear state [8,9]. Further basic demands placed on thermotropic materials are the exceptional high reversibility and reproducibility of the switching process along with homogeneous stability and low hysteresis [2,15]. A steep and rapid switching within a small temperature range is required [8,9]. Whereas the materials should be free of haze and coloring in the clear state, the turbidity in the scattering state should be distributed uniformly over the whole area, without appearance of streaks [15]. To obtain maximum light-shielding efficiency in the solar wavelength range (250–2500 nm) the scattering domain size should range between 200 and 400 nm in diameter and the differences in the refractive index between the scattering particles and the surrounding matrix should exceed 0.03 [1,11,20,55,66]. Fluid thermotropic materials, especially hydrogels, filled in the intervening space of a double glazing must show a high viscosity to distribute internal hydrostatic pressure and to not run out [2]. To achieve a high long-term stability the materials have to be stable against UV radiation, non-freezing and exhibit an excellent weatherability [2,15]. As to ecologic aspects thermotropic materials should be safely manageable, innocuously, low or non-flammable and free of

Table 4
Performance properties of thermotropic hydrogels, polymer blends and systems with fixed domains

Properties	Thermotropic hydrogels	Thermotropic polymer blends	Thermotropic systems with fixed domains
Switching temperature	5–60 °C	30–130 °C	25–100 °C
Highest solar transmittance in clear state	82%	>85%	84%
Maximum switching range and collector stagnation temperature according to switching range (determined for an all polymeric flat-plate collector with twin-wall sheet glazing and black absorber [8,9])	77% 75 °C	52% 90 °C	25% 125 °C
Reversibility	High	High	High
Reproducibility	High	n.a.	High
Homogeneous stability	High	n.a.	High
Hysteresis	Low	High	Low
Haze in clear state	Low	Low	High
Turbidity in opaque state	Uniform	Uniform	Uniform
Switching process	Steep	Gradual	Steep
Diameter of scattering domain	400–2500 nm	480 nm	>800 nm
Ageing and long-term stability	UV protection required; susceptible to dessication	Susceptible to humidity	Delamination
Ecologic aspects	Innocuously	Innocuously	Innocuously
Availability in large area	Yes	Yes	Yes
Costs	Expensive if synthetic materials used	No data available	Low
State of the art	Commercially available *Affinity Intelligent Window*™ [15]	No products available	With thermoplastic matrix: commercially available product developed by Buehler and Hewel [114] at EMS Chemie AG (CH) With crosslinked matrix: no products available

n.a. data not available.

organic solvents [2]. Furthermore, availability in a large area at low costs is essential [15].

3.1. Thermotropic hydrogels

Investigations on optical properties, switching properties, average particle size and distribution, long-term stability and ageing of thermotropic hydrogels for light-shielding applications are discussed extensively in the literature [1,4–6,10–12,14–16,18,21,25]. Other publications deal with outdoor tests and properties in practical applications such as façade elements, insulating glazing units and transparent insulation glazings [6,14,119,120].

The performance properties of thermotropic hydrogels are summarized in Table 4. In general, thermotropic hydrogels exhibit a high solar transmittance in the clear state ($>82\%$) and a high opacity (solar transmittance $<5\%$) in the scattering state. The materials show a steep switching gradient (<10 K) and a rapid and complete return to the transmitting state (low hysteresis) [4,5,15,16]. As to the switching temperature a flexible adjustment in the range between 5 and 60 °C is reported [4,15]. Differential light scattering measurements to characterize average sizes of structural inhomogeneities and thus scattering domain sizes for *Cloud Gel*$^{\text{TM}}$ and *TALD* reveal scattering particles up to 2500 nm in diameter [11]. The *Affinity Intelligent Window*$^{\text{TM}}$ exhibits particle sizes of $\sim$400 nm and retains a uniform state, even when heated partially [1,118]. As to economic aspects thermotropic hydrogels are quite expensive if synthetic materials are applied [18,21,25]. Hydroxypropylcellulose as a natural thermotropic material does not only enhance availability and environmental capability, but also decreases the costs for the functional material significantly (86–216 €/kg for synthetic materials; 4.60 €/kg for natural materials) [18,21,25]. However, the use of biopolymers requires a thorough protection against microorganisms [18,21,25]. Light and durability tests show that the switching range of the functional material used for the *Affinity Intelligent Window*$^{\text{TM}}$ decreases slightly, along with little yellowing of the sample and small air bubbles [14–16]. In general UV protection is required [14,15]. The *TALD* gel shows neither changes in the switching behavior nor in the optical properties in clear and cloudy state after 4000 cycles of heating [10]. Also some problems with water as a main component may arise, as water makes the thermotropic hydrogel susceptible to freezing and limits the operation temperature range to 0–40 °C [4]. The addition of anti-freezing agents depresses the freezing point to temperatures below −50 °C [4]. Furthermore thermotropic hydrogels filled into the intervening space of a double glazing, place high demands on sealing of the glazing. If not sealed properly the layer will dry out [3]. Reflection on the interfaces between the surrounding glazing and the thermotropic material may also cause a reduction in solar gains.

For the different thermotropic hydrogels developed to date commercialization was announced merely for the *Affinity Intelligent Window*$^{\text{TM}}$ [3]. In general, thermotropic hydrogels are well suited for solar thermal applications, as the high switching range of 77% would reduce maximum absorber temperatures to $\sim$75 °C, as shown by theoretical modeling of an all-polymeric flat-plate collector with twin-wall sheet glazing and black absorber (assuming 85% solar transmittance in clear state) [8,9]. This would allow for the application of cost-efficient plastics as absorber materials. Nevertheless, no thermotropic hydrogel is described currently that exhibits the working temperature range and switching temperatures required to provide adequate overheating protection for solar collectors. A further difficulty is that the only practical way of realizing overheating protection with thermotropic hydrogels to date is the encapsulation of the functional material between glass panes. This complex glazing configuration along with high mass is contradictory to the main aims of an all-polymeric solar collector such as simplifying design and reducing weight.

However, the basic properties such as transition temperature and working temperature range of thermotropic hydrogels can be adjusted for the application as overheating protection device in solar collectors. The switching temperature of the thermotropic hydrogel can be adapted by a change of the constituents and/or their concentration or, if the applied polymer consists of two or more monomer components, by a variation of the copolymer ratio. The composition of the solvent has great influence on the cloud point temperature. Furthermore, the switching temperature can be adjusted by the addition of surfactants or by coupling the hydrogel with alcohols, salts, acids or bases. Salts also affect viscosity and lead to a physical cross-linking of the system, which is advantageous for long-term stability. For thermotropic hydrogels formulated with water salts depress the freezing point and increase the boiling point of water and thus enhance durability and working temperature range. The durability of the system can be improved by the incorporation of molecular spacers. To enhance long-term performance for solar collector applications the replacement of water by other solvents may be advantageous. Alternatively the addition of anti-freezing agents is possible.

3.2. Thermotropic polymer blends

Thermotropic polymer blends are well examined in the literature. Some publications deal with switching characteristics and solar shading capability as a function of time, temperature and angle of incidence as well as with theoretical simulation experiments [4,5,17,22]. Other works focus on long-term stability and ageing optimization of thermotropic polymer blends as well as on practical applications [14,20,22].

As summarized in Table 4, thermotropic polymer blends exhibit a high solar transmittance ($>85\%$) in the clear state and a high opacity ($<38\%$) in the scattering state at elevated temperatures [4]. The switching temperature can be adjusted within a wide temperature range (30–130 °C) [4,108]. Goetzberger et al. [17] show that thermotropic polymer blends provide shading only at a solar position within ±30° relative to the south and an altitude of the sun between 30° and 65° (experiments performed at 48°N; orientation south; 30°inclination relative to the horizontal). Furthermore, the layers need several hours (up to 15 h) to become clear again completely (high hysteresis) [17]. Compared to hydrogels the time to reach the switching point is longer and the solar irradiation required to maintain the opaque state is higher [17]. Raicu et al. [22] demonstrate that the switching is very gradual in a temperature range of 40 °C and that especially at temperatures close to the switching point the reduction of the visible transmittance is more pronounced than the reduction of the solar transmittance. For this thermotropic polymer blend Fuchs [20] determined average scattering domain sizes of 480 nm in diameter. As to long-term stability it was observed that the temperature-dependent transmittance spectra were identical before and after the ageing test [14]. Nevertheless, the materials are very susceptible to humidity (transition to opaque state also at raised humidity levels) [14].

The developments on thermotropic polymer blends have been discontinued and no products are available at present [3]. Nevertheless, thermotropic polymer blends could provide adequate overheating protection for solar thermal systems. Assuming 85% solar transmittance in clear state, the switching range of 52% would reduce stagnation temperatures of an all-polymeric flat-plate collector with twin-wall sheet glazing and black absorber to

90 °C, which is the required maximum operating temperature for domestic hot water and space heating applications [8,9]. However, no materials with switching temperatures required for solar thermal applications have been realized so far. Further developments on thermotropic polymer blends should focus on the adjustment of switching temperatures between 55 and 80 °C. For the application in solar collectors also the long-term stability and performance of the materials have to be improved, especially with respect to the sensitivity to humidity. In this regard also an appropriate encapsulation of the blend may be an alternative.

There are several possibilities to adapt the properties of thermotropic polymer blends and thus to make them suited for solar collector applications. The switching temperature of the thermotropic system can be varied by a change of the interacting groups (polymers, copolymers) and/or their concentration, the change of the mobility and thus molecular weight of at least one polymer component (LCST decreases with increasing molecular weight) or the addition of substances with low molecular weight such as plasticizers (decrease of LCST). Numerous polymer blends exhibiting a LCST are given in Paul et al. [121]. Durability of the material itself can be enhanced by the addition of UV-stabilizers, antioxidants and/or weathering agents or by the formation of (semi)interpenetrating polymer networks, which also improve reversibility and affect the switching temperature. The switching performance can be tailored by adjusting the difference between the glass transition temperature of the homogeneously mixed polymer blend (below LCST) and the switching temperature or by varying the concentration of the mobile polymer component.

3.3. *Thermotropic systems with fixed domains*

TSFD are little discussed in the literature. Whereas Wilson gives a short overview, Resch and Wallner characterized thermotropic resins under polymer-physical aspects and established structure-property relationships [5,26]. In Resch et al. [27] a comprehensive spectroscopic characterization of TSFD is presented.

As discernible from Table 4, TSFD exhibit a solar transmittance (<85%) below the switching temperature which can be attributed to usually slight differences in the refractive indices between the components over the entire spectral range, which cause scattering also in the clear state [3,5,27]. As depicted in Resch et al. the turbidity in the opaque state is distributed uniformly over the whole area [27]. However, only moderate switching ranges up to 25% are reported [5,23,27]. Domain sizes exceeding 800 nm in diameter discussed so far do not allow for more effective shading in the solar spectral range [27]. Resch et al. [26] show that the switching temperature of TSFD can be adjusted in a wide temperature range by selecting adequate additives. In general the materials are characterized by a steep and rapid switching within a small temperature range <15 °C, a rapid and high reversibility and low hysteresis [26,27]. Functional layers can be produced environmental friendly and cost-efficient using existing polymer processing technologies (injection molding; extrusion; curing by UV radiation) and without the emission of polluting solvents [113,116,117]. For TSFD no research on long-term stability and ageing has been reported yet. Merely for layers laminated between glass panes, failure due to delamination is described [122].

Except the TSFD developed by Bühler et al. [113], no marketable products are available to date. The continuous utilization temperature of this material type ranges between 80 and 100 °C. The gradual transition from clear to cloudy of this TSFD, however, is not optimal for solar collector applications. In general, TSFD for autonomously shading glasses posses a high potential for industrial applications and active solar thermal systems. Theoretical modeling of an all-polymeric flat-plate collector (twin-wall sheet glazing; black absorber) with thermotropic overheating protection shows that even a moderate switching range of 25% would limit maximum absorber temperatures to ~125 °C (assuming 85% solar transmittance in clear state) [8,9]. The high reversibility and low hysteresis of TSFD are advantageous for overall solar thermal system efficiency. However, new developments should focus on the adjustment of appropriate switching temperatures and on the assurance of adequate durability. The switching properties of TSFD can be tailored easily for the desired application by selecting adequate additives. Information as to the switching process can be deduced from the thermal transition of the additive in advance. As the long-term stability of the thermotropic layer is strongly affected by the resin type and the cross-linking density, appropriate resin formulations have to be selected. Resins are available and already applied industrially that can withstand operating temperatures exceeding 100 °C. The long-term stability and weatherability can be improved further by adding stabilizers.

Especially the easy and fast adjustment of the switching temperature and high possible operating temperatures favor TSFD over thermotropic hydrogels and thermotropic polymer blends for the application in solar collectors. However, further research and development considering polymer physical parameters are necessary for optimizing product properties.

4. Summary and conclusions

Within this paper investigations and developments on thermotropic hydrogels, thermotropic polymer blends and thermotropic systems with fixed domains (TSFD) are reviewed with respect to requirements to prevent overheating of a solar thermal collector.

In general, thermotropic hydrogels are characterized by a high transparency in the clear state along with low haze and a change in solar transmittance by 77% at temperatures adjustable between 5 and 60 °C. The materials exhibit an excellent switching performance with a steep switching gradient, a high reversibility, and low hysteresis. Thermotropic hydrogels place high demands on UV protection and on sealing due to water as a main component and are expensive if synthetic materials are used. Thermotropic polymer blends undergo a transition from a highly transmitting state to a highly reflecting state (change in solar transmittance by 52%) at temperatures variable between 30 and 130 °C. These material types show a gradual switching within a broad temperature range along with high reversibility within a broad time-frame. Furthermore, the materials are susceptible to humidity. TSFD show a steep and rapid switching process within a small temperature range and an extraordinary high reversibility at low hysteresis. TSFD developed so far show a moderate change in transmittance (currently by 25%) above the switching threshold that is easily adjustable between 0 and 100 °C. The moderate switching performance of TSFD is related to an inappropriate size of the dispersed phase with particle diameters above 800 nm. Regarding the solar switching ranges, all material systems possess a high potential for solar thermal applications. For an all-polymeric flat-plate collector with twin-wall sheet glazing and black absorber thermotropic hydrogels, thermotropic polymer blends and TSFD would limit maximum absorber temperatures to 75, 90 and 125 °C, respectively (assuming 85% solar transmittance in clear state). The reduction of the maximum stagnation temperature to such temperatures would allow for the use of cost-efficient commodity plastics as absorber materials. However, the systems developed so far need to be adapted especially as to their switching temperatures required for solar thermal applications (55–60 °C, 75–80 °C) and optimized as to their long-term stability.

Acknowledgments

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH within the framework of the Non K_{plus} Program.

This work is funded by the State Government of Styria, Department *Zukunftsfonds Steiermark*.

References

[1] C.G. Granqvist, V. Wittwer, Materials for solar energy conversion: an overview, Sol. Energy Mater. Sol. Cells 54 (1998) 39–48.

[2] A. Seeboth, J. Schneider, A. Patzak, Materials for intelligent sun protecting glazing, Sol. Energy Mater. Sol. Cells 60 (2000) 263–277.

[3] P. Nitz, H. Hartwig, Solar control with thermotropic layers, Sol. Energy 79 (2005) 573–582.

[4] H.R. Wilson, Potential of thermotropic layers to prevent overheating—a review, SPIE 2255 (1994) 214–225.

[5] H.R. Wilson, Solar control coatings for windows, in: Grassie K., et al. (Eds.), Functional Materials—EUROMAT, vol. 13, Wiley VCH, Weinheim, pp. 221–233.

[6] A. Raicu, H.R. Wilson, Enhanced energy savings in buildings with thermotropic protection against overheating, in: Proceedings of Eurosun 1996, 16–19 September 1996, Freiburg, Germany, pp. 1297–1302.

[7] A. Khan, A. Brunger, Thermal protection of flat plate solar collectors using thermotropic glazings, in: Proceedings of 23rd Annual Conference of the Solar Energy Society of Canada Inc.: Implementing Sustainable Energy in a Changing World, 5–7 June 1997, Vancouver, Canada, pp. 119–124.

[8] K. Resch, R. Hausner, G.M. Wallner, All polymeric flat-plate collector—potential of thermotropic layers to prevent overheating, in: Proceedings of Solar World Congress 2007, 18–21 September 2007, Beijing, China, pp. 561–565.

[9] G.M. Wallner, K. Resch, R. Hausner, Property and performance requirements for thermotropic layers to prevent overheating in an all polymeric flat-plate collector, Sol. Energy Mater. Sol. Cells 92 (2008) 614–620.

[10] A. Beck, T. Hoffmann, W. Körner, J. Fricke, Thermochromic gels for control of insolation, Sol. Energy 50 (1993) 407–414.

[11] A. Beck, W. Körner, H. Scheller, J. Fricke, W.J. Platzer, V. Wittwer, Control of solar insolation via thermochromic light-switching gels, Sol. Energy Mater. Sol. Cells 36 (1995) 339–347.

[12] C.M. Lampert, Chromogenic switchable glazing: towards the development of the smart window, in: Proceedings of Window Innovations '95, 5–6 June 1995, Toronto, Canada.

[13] H. Watanabe, Intelligent window using a hydrogel layer for energy efficiency, SPIE 2531 (1995) 42–50.

[14] H.R. Wilson, A. Raicu, P. Nitz, Thermotropic materials and systems. Recent progress in a German joint project, in: Proceedings of Eurosun 1996, 16–19 September 1996, Freiburg, Germany, pp. 534–539.

[15] H. Watanabe, Intelligent windows using new thermotropic layers with long-term stability, Sol. Energy Mater. Sol. Cells 54 (1998) 203–211.

[16] A. Georg, W. Graf, D. Schweiger, V. Wittwer, P. Nitz, H.R. Wilson, Switchable glazing with a large dynamic range in total solar energy transmittance (TSET), Sol. Energy 62 (1998) 215–228.

[17] A. Goetzberger, M. Müller, M. Goller, A self regulating glare protection system using concentrated solar radiation and thermotropic coating, Sol. Energy 69 (2000) 45–57.

[18] J. Schneider, A. Seeboth, Natural thermotropic materials for solar switching glazing, Materialwissenschaft Werkstofftech. 32 (2001) 231–237.

[19] W. Eck, Reversibel entmischende Polymerblends mit temperaturabhängiger Lichttransmission, Ph.D. Thesis, Fakultät für Chemie und Pharmazie, Albert-Ludwigs-Universität Freiburg im Breisgau, 1993.

[20] K. Fuchs, Entwicklung und Charakterisierung thermotroper Polymerblends, Ph.D. Thesis, Fakultät für Chemie und Pharmazie, Albert-Ludwigs-Universität Freiburg im Breisgau, 2001.

[21] A. Seeboth, J. Kriwanek, D. Lötzsch, A. Patzak, Chromogenic polymer gels for reversible transparency and color control with temperature at a constant volume, Polym. Adv. Technol. 13 (2002) 507–512.

[22] A. Raicu, H.R. Wilson, P. Nitz, W. Platzer, V. Wittwer, E. Jahns, Facade systems with variable solar control using thermotropic polymer blends, Sol. Energy 72 (2002) 31–42.

[23] Informationsdienst BINE, Schaltbare und regelbare Verglasungen, 2002 〈http://www.bine.info/〉.

[24] H. Hartwig, Konzepte für die Integration selbstregelnder, thermotroper Schichten in moderne Gebäudehüllen zur passiven Nutzung der Sonnenenergie, Ph.D. Thesis, Fakultät für Architektur, Technische Universität München, 2003.

[25] A. Seeboth, J. Kriwanek, A. Patzak, D. Lötzsch, Chromogenic polymer gels for reversible transparency and color control, ACS Symp. Ser. 888 (2005) 110–121.

[26] K. Resch, G.M. Wallner, Thermotropic resin systems: relationships between formulation parameters, material structure and optical properties, in: Proceedings of Solar World Congress 2007, 18–21 September 2007, Beijing, China, pp. 541–545.

[27] K. Resch, G.M. Wallner, R.W. Lang, Spectroscopic investigations of phase-separated thermotropic layers based on UV cured acrylate resins, Macromol. Symp. (2007), in press. Q1

[28] N.A. Peppas, P. Bures, W. Leobandung, H. Ichikawa, Hydrogels in pharmaceutical formulations, Eur. J. Pharm. Biopharm. 50 (2000) 27–46.

[29] D. Schmaljohann, Thermo- and pH-responsive polymers in drug delivery, Adv. Drug Delivery Rev. 58 (2006) 1655–1670.

[30] K.-F. Arndt, T. Schmidt, R. Reichelt, Thermo-sensitive poly(methyl vinyl ether) micro-gel formed by high energy radiation, Polymer 42 (2001) 6785–6791.

[31] I. Dimitrov, B. Trzebicka, A.H.E. Mueller, A. Dworak, C.B. Tsvetanov, Thermosensitive water-soluble copolymers with doubly responsive reversibly interacting entities, Prog. Polym. Sci. 32 (2007) 1275–1343.

[32] G.W. Kühl, Mehrschichtenglas mit veränderlicher Lichtdurchlässigkeit und Verfahren zur Herstellung desselben, AT 179899, 1954.

[33] W. Falicoff, R. Delano, C.J. Raseman, Light transmitting or reflective sheet responsive to temperature variations, US 4877675, 1989.

[34] D. Chahroudi, Transparent thermal insulating system, US 3953110, 1976.

[35] D. Chahroudi, Solar control system, US 4307942, 1981.

[36] D. Chahroudi, Transparent infrared radiation absorption system, US 4389452, 1983.

[37] L. Starovoytova, J. Spevacek, Effect of time on the hydration and temperature-induced phase separation in aqueous polymer solution. 1H NMR study, Polymer 47 (2006) 7329–7334.

[38] E. Nies, T. Li, H. Berghmans, R.K. Heenan, S.M. King, Upper critical solution temperature phase behaviour, composition fluctuations, and complex formation in poly(vinyl methyl ether)/D2O solutions: small-angle neutron scattering in experiments and Wertheim lattice thermodynamic perturbation theory predictions, J. Phys. Chem. B 110 (2006) 5321–5329.

[39] E. Loozen, K. Van Durme, E. Nies, B. Van Mele, H. Berghmans, The anomalous melting behavior of water in aqueous PVME solutions, Polymer 47 (2006) 7034–7042.

[40] Y. Guo, Y. Peng, P. Wu, A two-dimensional correlation ATR-FTIR study of poly(vinyl methyl ether) water solution, J. Macromol. Struct. 875 (2008) 486–492.

[41] D. Chahroudi, Automatic light valves with polymeric layer containing network of bonds, US 5404245, 1995.

[42] H. Kröner, E. Jahns, M. Mielke, Gels having thermotropic properties, EP 0678534, 1995.

[43] R. Moerkeke, F. Meussen, R. Konigsveld, H. Berghmans, W. Mondelaers, E. Schacht, K. Dusekl, K. Solc, Phase transitions in swollen networks, 3. Swelling behavior of radiation cross-linked poly(vinyl methyl ether) in water, Macromolecules 31 (1998) 2223–2229.

[44] W. Reyntjens, L. Jonckheere, E. Goethals, F. Du Prez, Thermosensitive polymer structures based on segmented copolymer networks, Macromol. Symp. 164 (2001) 293–300.

[45] G.W. Kühl, Mehrschichtenglas, DE 1154905, 1964.

[46] G.W. Kühl, Light transmitting construction and process for its manufacture, US 3244582, 1967.

[47] T. Nonaka, T. Yoda, S. Kurihara, Swelling behavior of thermosensitive polyvinyl alcohol-graft-*N*-isopropylacrylamide copolymer membranes containing carboxyl groups and properties of their polymer solutions, J. Polym. Sci. Part A Polym. Chem. 36 (1998) 3097–3106.

[48] S. Aoshima, M. Ikeda, K. Nakayama, E. Kobayashi, H. Ohgi, T. Sato, Synthesis of poly(vinyl alcohol) graft copolymers by living cationic polymerization in the presence of added bases I. Design and synthesis of poly(vinyl alcohol) graft copolymers with well-controlled poly(vinyl ether) grafts, Polym. J. 33 (2001) 610. Q2

[49] W.-T. Wu, Y. Wang, L. Shi, Q. Zhu, W. Pang, G. Xu, F. Lu, Thermosensitive aqueous solutions of polyvinylacetone, Chem. Phys. Lett. 421 (2006) 367–372.

[50] T. Mitsumata, H. Kawada, J.I. Takimoto, Thermosensitive solutions and gels consisting of poly(vinyl alcohol) and sodium silicate, Mater. Lett. 61 (2007) 3878–3881.

[51] J. Byun, Y.M. Lee, C.-S. Cho, Swelling of thermosensitive interpenetrating polymer networks composed of poly(vinyl alcohol) and poly(acrylic acid), J. Appl. Polym. Sci. 61 (1996) 697–702.

[52] V. Boyko, S. Richter, A. Pich, K.-F. Arndt, Poly(*N*-vinylcaprolactam) microgels. Polymeric stabilization with poly(vinyl alcohol), Colloid Polym. Sci. 282 (2003) 127–132.

[53] S.J. Kim, S.J. Park, T.D. Chung, K.H. An, S.I. Kim, Properties of interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(*N*-isopropylacrylamide), J. Appl. Polym. Sci. 89 (2003) 2041–2045.

[54] J.-T. Zhang, S.-X. Cheng, R.-X. Zhuo, Poly(vinyl alcohol)/poly(*N*-isopropylacrylamide) semi-interpenetrating polymer network hydrogels with rapid response to temperature changes, Colloid Polym. Sci. 281 (2003) 580–583.

[55] O. Oktar, P. Caglar, W.R. Seitz, Chemical modulation of thermosensitive poly(*N*-isopropylacrylamide) microsphere swelling: a new strategy for chemical sensing, Sensors and Actuators B 104 (2005) 179–185.

[56] Y. Nishimura, S. Yuasa, M. Haruta, Y. Yoshinaga, H. Munakata, Optical element, US 4832466, 1989.

[57] V. Chytry, M. Netopilik, M. Bohdanecky, K. Ulbrich, Phase transition parameters of potential thermosensitive drug release systems based on polymers of *N*-alkylmethacrylamides, J. Biomater. Sci., Polym. Ed. 8 (1997) 817–824.

[58] D. Neradovic, W.L.J. Hinrichs, J.J. Kettenes-van den Bosch, W.E. Hennink, Poly(*N*-isopropylacrylamide) with hydrolysable lactic ester side groups: a new type of thermosensitive polymer, Macromol. Rapid Commun. 20 (1999) 577–581.

[59] L. Zhu, G. Zhu, M. Li, E. Wang, R. Zhu, X. Qi, Thermosensitive aggregates self-assembled by an asymmetric block copolymer of dendritic polyether and poly(*N*-isopropylacrylamide), Eur. Polym. J. 38 (2002) 2506–5203.

[60] X. Liu, L. Tang, Y. Dai, X. Wang, D. Liu, A novel polyurethane-modified poly(*N*-isopropylacrylamide) hydrogels, Polym. Adv. Technol. 13 (2002) 242–246.

[61] X.-M. Liu, L.-S. Wang, L. Wang, J. Huang, C. He, The effect of salt and pH on the phase transition behaviors of temperature-sensitive copolymers based on *N*-isopropylacrylamide, Biomaterials 25 (2004) 5659–5666.

[62] C.W. Park, S.M. Cho, B.K. Kim, Synthesis and properties of thermosensitive polyurethane-b-poly(*N*-isopropylacrylamide), React. Funct. Polym. 66 (2006) 585–591.

[63] L.M. Geever, D.M. Devine, M.J.D. Nugent, J.E. Kennedy, J.G. Lyons, A. Hanley, C.L. Higginbotham, Lower critical solution temperature control and swelling behaviour of physically crosslinked thermosensitive copolymers based on *N*-isopropylacrylamide, Eur. Polym. J. 42 (2006) 2540–2548.

[64] Y. Zhang, S. Kato, T. Anazawa, A flat-type hydrogel actuator with fast response to temperature, Smart Mater. Struct. 16 (2007) 2175–2182.

[65] H.K. Ju, S.Y. Kim, S.J. Kim, Y.M. Lee, pH/temperature-responsive semi-IPN hydrogels composed of alginate and poly(*N*-isopropylacrylamide), J. Appl. Polym. Sci. 83 (2001) 1128–1139.

[66] S.J. Kim, C.K. Lee, Y.M. Lee, S.I. Kim, Preparation and characterization of thermosensitive poly(*N*-isopropylacrlyamide)/poly(ethylene oxide) semi-interpenetrating polymer networks, J. Appl. Polym. Sci. 90 (2003) 3032–3036.

[67] K.F. Mueller, Thermotropic copolymer hydrogels from *N*,*N*-diemthylacrylamide and methoxy-ethyl (meth)acrylate, US 5057560, 1991.

[68] K.F. Mueller, Thermotropic biphilic hydrogels and hydroplastics, EP 0311566, 1993.

[69] G.W. Kühl, Lichtdurchlässiger Körper variabler Transparenz, DE 2154042, 1981.

[70] M. Eisele, W. Burchard, Hydrophobic water-soluble polymers, 1. Dilute solution properties of poly(1-vinyl-2-piperidone) and poly(*N*-vinylcaprolactam), Die Makromolekulare Chemie 191 (1989) 169–184.

[71] E.E. Makhaeva, L.T.M. Than, S.G. Starodoubtsev, A.R. Khokhlov, Thermoshrinking behaviour of poly(vinylcaprolactam) gels in aqueous solution, Macromol. Chem. Phys. 197 (1996) 1973–1982.

[72] F. Meeussen, E. Nies, H. Berghmans, S. Verbrugghe, E. Goethals, F. Du Prez, Phase behaviour of poly(*N*-vinyl caprolactam) in water, Polymer 41 (2000) 8597–8602.

[73] S. Verbrugghe, A. Laukkanen, V. Aseyev, H. Tenhu, F.M. Winnik, F.E. Du prez, Light scattering and microcalorimetry studies on aqueous solutions of thermo-responsive PVCL-g-PEO copolymers, Polymer 44 (2003) 6807–6814.

[74] Y. Gao, S.C.F. Au-Yeung, C. Wu, Interaction between surfactant and poly(*N*-vinylcaprolactam) microgels, Macromolecules 32 (1999) 3674–3677.

[75] H. Vihola, A. Laukkanen, J. Hirvonen, H. Tenhu, Binding and release of drugs into and from thermosensitive poly(*N*-vinyl caprolactam) nanoparticles, Eur. J. Pharma. Sci. 16 (2002) 69–74.

[76] R. Rullier, Multiple panes, GB 1541372, 1977.

[77] R. Rullier, Verglasung mit veränderlicher Transparenz, DE 2658643, 1977.

[78] W.E. Walles, W.F. Tousignant, Water-soluble copolymers of ring-substituted *N*-vinyl-2-oxazolidinone, US 2946772, 1960.

[79] W.E. Walles, Energy saving radiant insulative device, US 4260225, 1981.

[80] H. Uyama, S. Kobayashi, A novel thermo-sensitive polymer. Poly(2-iso-propyl-2-oxazoline), Chem. Lett. 9 (1992) 1643–1646.

[81] H. Okamura, T. Maruyama, S. Masuda, K. Minagawa, T. Mori, M. Tanaka, A novel thermosensitive poly(methyl 2-acetamidoacrylate), J. Polym. Res. 9 (2002) 17–21.

[82] H. Okamura, T. Mori, K. Minagawa, S. Masuda, M. Tanaka, A novel thermosensitive polymer, poly(methyl 2-propionamidoacrylate) with geminal substituents, Polymer 43 (2002) 3828–3852.

[83] H. Okamura, S. Masuda, K. Minagawa, T. Mori, M. Tanaka, Thermosensitive properties of a novel poly(methyl 2-acetamidoacrylate-co-methyl acrylate), Eur. Polym. J. 38 (2002) 639–644.

[84] T. Mori, Y. Fukuda, H. Okamura, K. Minagawa, S. Masuda, M. Tanaka, Thermosensitive copolymers having soluble and insoluble monomer units, poly(*N*-vinylacetamide-co-methyl acrylate)s: effect of additives on their lower critical solution temperatures, J. Polym. Sci. Part A Polym. Chem. 42 (2004) 2651–2658.

[85] T. Mori, M. Hamada, T. Kobayashi, H. Okamura, K. Minagawa, S. Masuda, M. Tanaka, Effect of alkyl substituents structures and added ions on the phase transition of polymers and gels prepared from methyl 2-alkylamidoacrylates, J. Polym. Sci. Part A Polym. Chem. 43 (2005) 4942–4952.

[86] J.H. Lee, D.G. Bucknall, Swelling behaviour and network structure of hydrogels synthesized using controlled UV-initiated free radical polymerization, J. Polym. Sci. Part B Polym. Phys. 46 (2008) 1450–1462.

[87] K. Suwa, K. Morishita, A. Kishida, M. Akashi, Synthesis and functionalities of poly (*N*-vinylalkylamide), V. Control of a lower critical solution temperature of poly(*N*-vinylaklyamide), J. Polym. Sci. Part A Polym. Chem. 35 (1997) 3087–3094.

[88] K. Suwa, Y. Wada, A. Kishida, M. Akashi, Synthesis and functionalities of poly (*N*-vinylalkylamide), Synthesis and functionalities of poly (*N*-vinylalkylamide), VI. Novel thermosensitive hydrogel crosslinked poly(*N*-vinylisobutyramide), J. Polym. Sci. Part A Polym. Chem. 35 (1997) 3377–3384.

[89] A. Kishida, Y. Kikunaga, M. Akashi, Synthesis and functionalities of poly (*N*-vinylalkylamide), Synthesis and functionalities of poly (*N*-vinylalkylamide), X. A novel aqueous two-phase system based on thermosensitive polymers and dextran, J. Appl. Polym. Sci. 73 (1999) 2545–2548.

[90] K. Yamamoto, Y. Imamura, E. Nagatoma, T. Serizawa, Y. Murakoa, M. Akashi, Synthesis and functionalities of poly (*N*-vinylalkylamide), XIV. Polyvinylamine produced by hydrolysis of poly(*N*-vinylformamide) and its functionalization, J. Appl. Polym. Sci. 89 (2003) 1277–1283.

[91] K. Yamamoto, T. Serizawa, Y. Murakoa, M. Akashi, Synthesis and functionalities of poly (*N*-vinylalkylamide), XII. Synthesis and thermosensitive property of poly(vinylamine) copolymer prepared from poly(*N*-vinylformamide-co-*N*-vinylisobutyramide), J. Polym. Sci. Part A Polym. Chem. 38 (2000) 3674–3681.

[92] W. Lin, M. Hu, Y.-L. Hsieh, M.J. Kurth, J.M. Krochta, Thermosensitive lactitol-based polyether polyol (LPEP) hydrogels, J. Polym. Sci. Part A Polym. Chem. 36 (1998) 979–984.

[93] C. Dworak, B. Trzebicka, W. Walach, A. Utrata, C. Tsvetanov, Novel reactive thermosensitive polyethers—control of transition point, Macromol. Symp. 210 (2004) 419–426.

[94] M. Jamroz-Piegza, A. Utrata-Wesolek, B. Trzebicka, A. Dworak, Hydrophobic modification of high molar mass polyglycidol to thermosensitive polymers, Eur. Polym. J. 42 (2006) 2497–2506.

[95] L. Bösing, P. Grünberg, H. Riemer, W. Friedrich, T. Pollok, Process for preparing a polymer matrix with temperature-dependent haze, EP 0677536, 1995.

[96] G.M. Campese, E.M.G. Rodrigues, E.B. Tambourgi, A. Pessoa, Determination of cloud point temperatures for different copolymers, Brazilian J. Chem. Eng. 20 (3) (2003).

[97] M.J. Song, D.S. Lee, J.H. Ahn, D.J. Kim, S.C. Kim, Thermosensitive sol–gel transition behaviors of poly(ethylene oxide)/aliphatic polyester/poly(ethylene oxide) aqueous solutions, J. Polym. Sci. Part A Polym. Chem. 42 (2004) 772–784.

[98] T. Mori, Y. Shiota, K. Minagawa, M. Tanaka, Alternative approach to the design of thermosensitive polymers: the addition of hydrophobic groups to the ends of hydrophilic polyether, J. Polym. Sci. Part A Polym. Chem. 43 (2005) 1007–1013.

[99] S. Meinhardt, Thermal-translucid gel, method for its preparation and utilization thereof, EP 0228422, 1986.

[100] D.D. Howard, M.L. Nulph, Thermosensitive polymer compositions and films, GB 2095271, 1982.

[101] D.J. Zalucha, F.H. Sexsmith, D.D. Howard, M.L. Nulph, Thermally-responsive polymeric materials, US 4409383, 1983.

[102] G.W. Kühl, Verfahren zur Herstellung eines Mehrschichtenglases mit veränderlicher Lichtdurchlässigkeit, DE 1012752, 1958.

[103] T. Tanaka, Y. Hirokawa, Volume phase transition in a nonionic gel, J. Chem. Phys. 81 (1984) 6379–6380.

[104] R.B. Stephens, Temperature responsive optical switch, US 4261331, 1981.

[105] H. Watanabe, Laminate controlling light autonomously and window using the same, EP 1655357, 2006.

[106] Q. Zhou, L. Zhang, M. Minoda, T. Miyamoto, Phase transition of thermosensitive amphiphilic cellulose esters bearing olig(oxyethylene)s, Polym. Bull. 45 (2000) 381–388.

[107] W. Siol, H.J. Otto, U. Terbrack, Temperature-variable light transmission vitrifications, EP 0181485, 1993.

[108] W. Eck, H.J. Cantow, V. Wittwer, Material with temperature dependent light transmission, EP 0559113, 1993.

[109] E. Jahns, H. Kröner, W. Schrof, U. Klowdig, Cross-linked polymer systems, EP 0749465, 1995.

[110] A. Kleinke A, T. Kessler, E. Jahns, Temperature control radiation transmission material, US 6379769, 1999.

[111] E. Jahns, I. Kühn, T. Liese-Sauer, W. Abicht, Thermotropic greenhouse films, EP 1218467, 2001.

[112] W. Dabisch, Body with reversibly changeable temperature dependent extinction of light and method for the manufacture of this body, EP 0000868, 1978.

[113] F.S. Buehler, M. Hewel, Reversible thermotropic composition, its preparation and use, EP 0985709, 1999.

[114] S. Meinhardt, U. Schönfeld, H. Gödeke, Thermo-optical polymer material providing reversible shading, DE 4433090, 1996.

[115] T. Bicer, H. Gödeke, J. Werner, U. Schönfeld, Method for producing a thermooptical variable polymerized material, and use of same, EP 0946443, 1997.

[116] T. Bicer, C. Schwitalla, H. Gödeke, Method for producing thermotropic casting resin systems, EP 1095080, 1999.

[117] C. Schwitalla, H. Gödeke, H. König, Thermotropic foil and method of manufacturing the same, EP 1258504, 2002.

[118] P. Nitz, Optische Modellierung und Vermessung thermotroper Systeme, Ph.D. Thesis, Fakultät für Physik, Albert-Ludwigs-Universität Freiburg im Breisgau, 1999.
[119] T. Inoue, Solar shading and daylighting by means of autonomous responsive dimming glass: practical application, Energy Build. 35 (2003) 463–471.
[120] T. Inoue, M. Ichinose, N. Ichikawa, Thermotropic glass with active dimming control for solar shading and daylighting, Energy Build., in press. **Q3**
[121] D.R. Paul, J.W. Barlow, R.E. Bernstein, D.C. Wahrmund, Polymer blends containing poly(vinylidene fluoride), Part IV: Thermodynamic interpretations, Polym. Eng. Sci. 18 (1978) 1225–1234.
[122] Informationsdienst BINE, Information notes, 2005 〈http://www.bine.info/〉.

3 Investigation of Matrix Materials for Thermotropic Systems with Fixed Domains

3.1 Introduction

Among different thermo-functional materials, thermotropic systems with fixed domains (TSFD) possess the highest potential for overheating protection applications in solar collectors (Resch and Wallner, 2008). This can be attributed to their distinct advantages such as the easy adjustment of the switching threshold, high possible operating temperatures, high reversibility and low hysteresis. In TSFD scattering domains are embedded statically in a polymer matrix material (e.g. Seeboth et al., Wilson, 2000; 2000; Nitz, 2005;). Although also thermoplastic matrices are considered in the literature (Dabisch, 1978; Buehler, 1999), most publications deal with cross-linked matrices, and thus thermoset resins (Dabisch, 1978; Meinhardt et al., 1996; Bicer et al., 1997; Bicer et al., 2000; Schwitalla et al., 2002; Wilson, 2000). Especially for preliminary tests and basic material development, thermoset resins are favourable to thermoplastics, because the incorporation of scattering particles in thermosets is more flexible and requires less processing effort.

Due to higher polymerization rates, lower temperatures of curing and the solvent free formulation, resin systems curable by energetic radiation, especially by ultraviolet (UV) light, are favored to thermally curing material types for the production of TSFD (Bicer et al., 2000; Schwitalla et al., 2002). In a UV-curable resin, UV energy from a light source causes the photoinitiator to fragment into reactive species. These species (either free radical or cationic) react with unsaturated monomers/oligomers in the resin formulation and thus initiate a cross-linking reaction that converts the liquid into a cured film (Fouassier, 1995; Fouassier 1997; Beck, 2002).

A UV-curable resin consists of three main components – the oligomer, a monomer, which is mostly referred to as reactive diluent, and a photoinitiator. The oligomer is a multifunctional material which gives a cross-linking polymerization. Acrylate functional groups were found to be most effective. The backbone of the oligomer plays a decisive role for the final properties of the film. Most commonly applied are epoxy, urethane, or polyester acrylates. A reactive diluent is a low molecular weight acrylate monomer with double bond functionalities, which is added to adjust the system viscosity. This monomer participates in the polymerization reaction and becomes part of the polymer matrix in the cured resin. If large concentrations are added, the influence of the reactive diluent on the performance properties of the system can be significant. The photoinitiator system is responsible for the free radical formation and is thus the critical component of the UV curing process. The selection of an adequate photoinitiator formulation depends on the resin type and application (Fouassier, 1995; Fouassier 1997; Beck, 2002).

The curing rate, degree of cure, and performance properties of the resin system are directly affected by the concentration of its constituents (Fouassier, 1995; Fouassier 1997; Lecamp et al., 1997; Ruiz et al., 2003). Thus, in order to optimize a resin formulation for a given application, extensive tests and experiments are necessary. For the reflectance efficiency of a TSFD in the scattering state especially the cross-linking characteristics of the matrix material are playing a key role (Bicer, 1997). High curing rates are essential to maintain a homogeneous additive distribution. Cross-linking densities and glass transition temperatures affect the precipitation of the additive and are advantageous for the long-term stability (Resch et al., 2008). In summary, besides the chemical backbone the evaluation of resin formulations for the production of TSFD must consider

- the curing rate,
- the degree of cure, and
- the glass transition temperature.

TSFD reported so far were not developed regarding cross-linking characteristics, polymer-physical properties, and formulation parameters of the resin material. Furthermore material selection was not described to be done according to the degree of cure and the glass transition temperature of the matrix material. Thus, within this chapter an approach for the determination of relevant cross-linking parameters and matrix properties of a UV-curable resin is presented. Emphasis is placed on the effect of the concentrations of oligomer, reactive diluent and photoinitiator on the curing characteristics and the final degree of cure of a UV-curable resin. Conclusions concerning the suitability of the resin formulations for the preparation of TSFD are drawn.

For this study materials were provided by Cytec Surface Specialties (Drogenbos, BE). The oligomer used is an aliphatic urethane diacrylate (difunctional). The reactive diluent added is 1,6 hexanediol diacrylate. A liquid radical photoinitiator blend based on 1-hydroxy-cyclohexylphenyl-ketone and benzophenone is chosen. The concentrations of reactive diluent (x=30, 40, 50 m%), photoinitiator (y=2, 3, 4, 5 m%) and oligomer (100-x-y m%) are varied.

3.2 Paper 2

Paper 2: Cross-linking behavior of UV-curable acrylate resins
by K. Resch, G.M. Wallner and R.W. Lang
(to be published in: *Journal of Plastics Technology*)

This paper includes an investigation concerning the effect of resin formulation on the curing characteristics and properties of a UV-curable acrylate polymer. The cross-linking process is studied applying real-time cure monitoring by Dielectric Analysis (DEA). A quantitative evaluation of the degree of cure is performed applying Attenuated Total Reflectance Spectroscopy (ATR). The glass transition temperature is deduced from thermo-mechanical measurements by Dynamic Mechanical Analysis (DMA).

3.3 Key Literature

Beck, E. (2002). Rohstoffe fuer radikalisch strahlungshärtbare Systeme' Skriptum zu UV-Seminar Esslingen, DE.

Bicer, T., Goedeke, H., Werner, J., Schoenfeld, U. (1997). EP 0946443.

Bicer, T., Schwitalla, C., Goedeke, H. (2000). EP 1095080.

Buehler, F. S., Hewel, M. (1999). EP 0985709.

Dabisch, W. (1978). EP 0000868.

Fouassier, J.P. (1995). Photoinitiation, Photopolymerization and Photocuring, Hanser, Munich.

Fouassier, J.P. (1997). In "Radiation curing in polymer science and technology", (Fouassier, J.P. and Rabek, J.F. , Eds), Vol. 1, pp 49-117, Elsevier, London.

Lecamp, L., Youssef, B., Bundel, C., Lebaudy, P. (1997). Polymer **38**, 6089.

Meinhardt, S., Schoenfeld, U, Goedeke, H. (1996). DE 4433090.

Nitz, P., Hartwig, H. (2005). Solar Energy **79**, 573.

Resch, K., Wallner, G.M. (2008). Solar Energy Materials and Solar Cells, corrected proof, in press.

Resch, K., Wallner, G.M., Hausner, R. (2008). Submitted to Solar Energy (Paper 5 within this dissertation).

Ruiz, C.S.B., Machado, L.D.B., Volponi, J.E., Pino, E.S. (2003). Nuclear Instruments and Methods in Physics Research B **208**, 309.

Schwitalla, C., Goedeke, H., Koenig, H. (2002). EP 1258504.

Seeboth, A., Schneider, J., Patzak, A. (2000). Solar Energy Materials and Solar Cells **60**, 263.

Wilson, H.R. (2000). Functional Materials – EUROMAT 99 **13**, 221.

Zeitschrift Kunststofftechnik
Journal of Plastics Technology

WAK
Wissenschaftlicher Arbeitskreis der Universitäts-Professoren der Kunststofftechnik

archival, peer-reviewed online Journal of the Scientific Alliance of Polymer Technology
archivierte, peer-rezensierte Internetzeitschrift des Wissenschaftlichen Arbeitskreises Kunststofftechnik (WAK)
www.plasticseng.com, www.kunststofftech.com

handed in/eingereicht: 27.05.2008
accepted/angenommen: xx.xx.20xx

Katharina Resch[1], Gernot M. Wallner[2], Reinhold W. Lang[1,2]
1) Polymer Competence Center Leoben GmbH
2) Institute of Materials Science and Testing of Plastics, University of Leoben

Cross-linking behavior of UV-curable acrylate resins

Within this study the effect of the concentrations of oligomer, reactive diluent and photoinitiator on the cross-linking characteristics of UV-curable urethane acrylate polymers was analyzed applying dielectric analysis (DEA), Attenuated Total Reflectance Spectroscopy (ATR spectroscopy) and Dynamic Mechanical Analysis (DMA). Real-time cure monitoring by DEA provided fundamental information on the progress of polymerization and polymerization rate. A significant effect of the ambient temperature on the curing characteristics was discernible. An influence of the concentrations of photoinitiator and reactive diluent on the curing rate and time was not observable. After a curing time of 230 seconds the various resin formulations exhibited degrees of cure between 0.96 and 0.99. ATR spectroscopy ascertained that the degree of conversion on the surface exposed to air during the curing process is enhanced by increased photoinitiator concentrations. DMA revealed glass transition temperatures between 16 and 21°C for the different materials.

Vernetzungsverhalten UV-härtender Acrylat-harze

In dieser Studie wurde der Einfluss des Anteils an Oligomer, Reaktivverdünner und Photoinitiator auf die Vernetzungseigenschaften UV-härtender Acrylatharze mittels Dielektrischer Analyse (DEA), Attenuated Total Reflectance Spektroskopie (ATR-Spektroskopie) und Dynamisch Mechanischer Analyse (DMA) charakterisiert. Mittels DEA wurden Informationen hinsichtlich des Polymerisationsfortschritts und der Vernetzungsgeschwindigkeit abgeleitet. Die Umgebungstemperatur wirkte sich signifikant auf das Reaktionsverhalten der Harze aus. Polymerisationsgeschwindigkeit und -zeit wurden nicht von der Konzentrationen an Photoinitiator und Reaktivverdünner beeinflusst. Nach einer Bestrahlungszeit von 230 Sekunden wurden Vernetzungsgrade zwischen 0.96 und 0.99 erreicht. Über ATR-Spektoskopie wurde belegt, dass sich der Umsatz an der Oberfläche durch höhere Anteile an Photoinitiator verbessert. Untersuchungen mittels DMA zeigten, dass die Glasübergangstemperaturen der verschiedenen Harzformulierungen zwischen 16 und 21°C liegen.

Cross-linking behavior of UV-curable acrylate resins

Katharina Resch, Gernot M. Wallner, Reinhold W. Lang

1 INTRODUCTION

Thermotropic resins are actively switchable layers which change their light transmission behavior from highly transparent to light diffusing upon reaching a certain threshold temperature reversibly [1-9]. The autonomous shading is induced by a sudden change in the refractive index of scattering particles, which are statically embedded in a matrix material [5,7-9]. Such functional films can provide overheating protection for passive solar thermal systems (e.g., glazings in buildings) as well as for active solar thermal systems (e.g., hot water collectors) [5,7,10-15].

Due to distinct advantages such as the high polymerization rate, the low temperature of curing and the solvent free formulation UV-curable acrylate functionalized polymers and oligomers are used currently for thermotropic resins [3,6,8,9]. UV-curable resins are typically composed of a photoinitiator, a low viscous reactive diluent and a reactive acrylate oligomer, which determines the application properties [16,17]. Thermotropic layers are produced by dissolving a thermotropic additive in the resin material initially [1-3,6,8,9]. The subsequent cross-linking process causes the additive component to precipitate, which results in the formation of scattering domains [1-3,6]. As the scattering particle size and distribution directly affects the reflectance efficiency of the thermotropic material in the opaque state, the dissolving power and the curing characteristic of the matrix material are playing a key-role in the performance of a thermotropic resin [3]. High curing rates are essential to maintain a homogeneous additive distribution, especially for systems which are prepared at temperatures exceeding the curing temperature [3]. Increased cross-linking densities and high glass transition temperatures may favor the precipitation of the additive in the desired dimension and the long-term stability [18]. The cross-linking characteristics of the resin system are directly affected by the concentration of its components [16,17,19-21].

Hence, the main objective of the present paper is to perform a systematic investigation of the effect of the concentrations of oligomer, reactive diluent and photoinitiator on the cross-linking characteristics of UV-curable urethane acrylate resins. Both, surface and bulk sensitive characterization techniques are applied. Specific focus is given to the potential of real-time cure monitoring by dielectric analysis (DEA) to study curing rate and state of cure. In addition, by Attenuated Total Reflectance Spectroscopy (ATR spectroscopy) the degree of conversion is evaluated. Results are compared to the degree of cure of the bulk deduced from the glass transition temperature determined by Dynamic Mechanical Analysis (DMA).

2 EXPERIMENTAL

2.1 Materials

The prepolymer used was an aliphatic urethane diacrylate (difunctional) diluted with 12% of 1,6 hexanediol diacrylate (HDDA) monomer. To adjust system viscosity difunctional HDDA was selected. A liquid radical photoinitiator blend based on 1-hydroxy-cyclohexylphenyl-ketone and benzophenone was chosen to initiate the photo-polymerization process. UV-curable resins were prepared by mixing the components at room temperature. Various material formulations were produced by systematically varying the concentration of reactive diluent (x=30, 40, 50 wt.%), photoinitiator (y=2, 3, 4, 5 wt.%) and oligomer (100-x-y wt.%).

2.2 Dielectric Analysis (DEA)

Dielectric measurements were carried out using a dielectric analyzer DEA 231/1 (Netzsch-Gerätebau GmbH, Selb, GER) at a frequency of 1000 Hz and a data acquisition rate of 0.1 s. All experiments were performed using nickel plated interdigitated electrode sensors on a polyimide substrate (65S, A/D ratio 80, electrode spacing 125 µm (Netzsch-Gerätebau GmbH, Selb, GER)). The resin formulation was applied to the sensor with a paint-brush. A spacer allowed for the adjustment of a constant wet-film thickness of 600 µm. The curing reaction was induced by a UV-lamp featuring a radiant power of 13.6 W in the UV-A and 3 W in the UV-B wavelength region (Ultra-Vitalux, OSRAM GmbH, München, GER). The light curing device was assembled 5 cm above the specimen. To investigate the effect of the curing setup on the photopolymerization process for one material formulation, a sample-lamp distance of additional 25 cm was implemented. The irradiation was maintained for 230 s. All experiments were performed at ambient temperature in the presence of air. Logarithmic plots of the ion viscosity as a function of curing time were analyzed as to minimum and maximum ion viscosity. In addition, the maximum slope was determined, which is a measure for the conversion rate [22,23]. The data presented below have been averaged over three measurements.

2.3 Attenuated Total Reflectance Spectroscopy (ATR spectroscopy)

The degree of cure was determined applying Fourier Transform Infrared (FT-IR)-spectroscopy in Attenuated Total Reflectance mode. A Perkin Elmer

Spectrum GX (Perkin Elmer Instruments GmbH, Überlingen, GER) IR spectrophotometer equipped with a Pike MIRacle Micro ATR (Pike Technologies, Madison, USA) was used. Spectra were recorded on uncured resins as well as on both surfaces of photo-cured samples from DEA (top surface: surface facing air; bottom surface: surface facing the dielectric sensor) within a wavenumber range from 700 to 4000 cm^{-1} at a resolution of 1 cm^{-1}. For each material formulation, sample surface measurements were repeated four times. The acrylate conversion X was deduced from the IR absorbance areas at 810 cm^{-1} (vinyl unsaturations), before (A_0) and after (A_t) UV-irradiation according to $X = 1 - A_t/A_0$ [24]. For this quantitative evaluation the recorded spectra were corrected for the wavelength-dependent penetration depth of the evanescent wave as well as for the baseline by the Spectrum v. 5.0 software (Perkin Elmer Instruments GmbH, Überlingen, GER). Afterwards the spectra were normalized for 100% absorption at 2862 cm^{-1}, characteristic for H-C-H stretching vibrations [24].

2.4 Dynamic Mechanical Analysis

Thermo-mechanical properties of films produced from the different resin formulations were characterized by dynamic mechanical analysis (DMA) on a DMA861e (Mettler Toledo GmbH, Schwarzenbach, CH). For each material formulation two rectangular specimens (30x5x0.5-0.6 mm) were punched out from photo-cross-linked samples from DEA-experiments. DMA was carried out in a tensile mode applying a constant sinusoidal strain amplitude of 20 µm at a frequency of 1 Hz. The gauge length was 19.5 mm. Scans were run in a temperature range from -30 to 150°C at a heating rate of 3K/min. From DMA storage modulus (E’), loss modulus (E’’) and loss factor (tanδ) curves were generated as a function of film temperature. The temperature where the maximum in loss modulus occurs was taken as the glass transition temperature, which is a qualitative measure for the degree of cure [25]. As numerous samples failed before reaching the rubbery region, a quantitative evaluation of the cross-linking density by the theory of rubber elasticity for a Gaussian network was not possible.

3 RESULTS AND DISCUSSION

3.1 Dielectric Analysis (DEA)

In Fig. 1 the ion viscosity curves for a resin formulation containing 40 wt.% reactive diluent and 3 wt.% photoinitiator photo-polymerized at distances of 25 and 5 cm to the UV lamp are compared. In general the sample cured at the lower distance to the UV light source exhibits a steeper increase of the ion viscosity and thus a higher polymerization rate. For this sample also the plateau of the ion viscosity which is an indication for the progress of polymerization is already reached after an irradiation time of 30 seconds. The ion viscosity of the sample cross-linked at the lower distance to the lamp decreases again after a plateau between 30 and 40 seconds irradiation time. This decrease can be attributed to an increase of the sample temperature due to heat evolved by the UV lamp, which enhances ion mobility. Temperature measurements showed that the ambient temperature at the sample position exceeds 90°C after a curing time of 40 seconds. The ion viscosity for the sample cured at the higher distance to the lamp levels up after an irradiation time of 120 seconds. At the higher distance between sample and light source the ambient temperature remains below 40°C over the whole curing process only slightly increasing with increasing curing time. These moderate curing temperatures do not affect the characteristics of the ion viscosity, as it reaches a final plateau for this photo-polymerization setup. Nevertheless, the obtained maximum values of the ion viscosity are not affected by the sample-lamp distance.

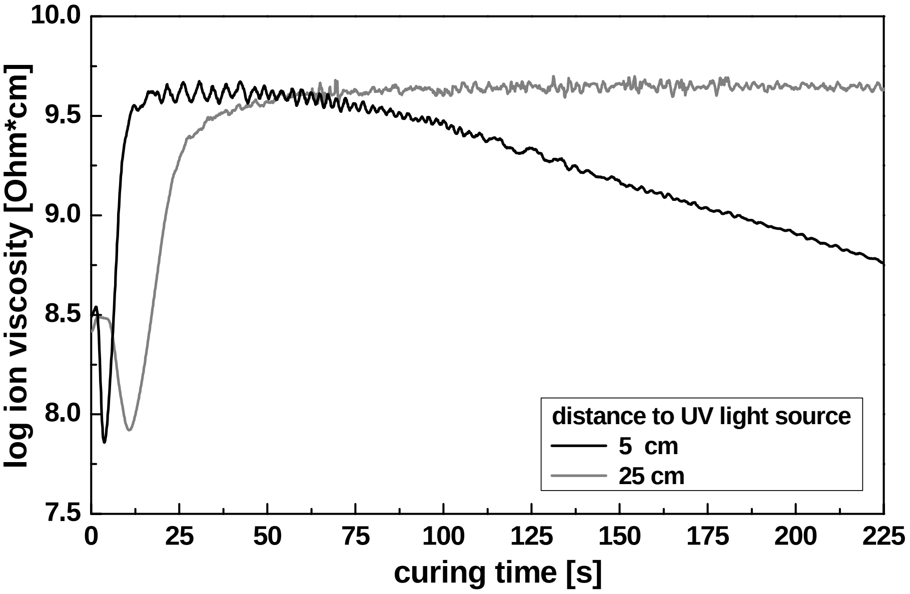


Fig. 1: Ion viscosity as a function of the curing time for a resin formulation containing 40 wt.% reactive diluent and 3 wt.% photoinitiator for sample-lamp distances of 5 cm and 25 cm

In a study of Lecamp et al. [20], polymerization rate and degree of cure were found to be favored by sample temperatures slightly above the glass transition temperature of the resulting material and below the thermal polymerization temperature. In addition, an increase of curing rate and ultimate conversion with enhanced irradiation was observed. Applying dielectric cure monitoring, Stampfer and Ehrenstein [26] described an increase of the cure velocity with an increase of the light intensity from 25 to 50 mW/cm^2. Smith and O'Malley [23] detected significant higher levels of the ion viscosity, and thus higher degrees of conversion at increased curing intensities. The applied UV lamp powers varied between 100 and 300 W. The differences in irradiation power are much lower within the present study. Thus, the differing UV intensities may have a minor impact on the final degree of cure as well as on the curing rate. The detected variations in curing rate can rather be attributed to the different temperature conditions. However, for both curing conditions the temperature exceeds the glass transition temperature of the resulting material, which is about 20°C (determined by DMA). Furthermore, DSC measurements revealed that neither evaporation of reactants and photoinitiator degradation nor thermal polymerization of the resin formulation occur in the temperature range between 0°C and 150°C. Thus, the effect of the temperature conditions on the overall degree of conversion is expected to be weakly pronounced.

The data presented in the following have been recorded at a distance of 5 cm between sample and UV light source. In Fig. 2 the maximum slope of the investigated resin formulations is plotted as a function of the photoinitiator concentration for various amounts of reactive diluent added. The maximum slope of the DEA curve provides information about the polymerization rate. In general the polymerization rate of the resins is not affected by the concentrations of photoinitiator and reactive diluent. For the various material formulations the time to yield inversion point was 8 seconds. A high mean deviation in data is observable, especially for resins formulated with 40 and 50 wt.% reactive diluent. Conversion rate appears to be very sensitive to wet film thickness. Slight differences in film thickness were detected after curing, which are more pronounced for materials containing higher amounts of reactive diluent. This indicates that preservation of a constant wet film thickness is complicated by a decreased viscosity.

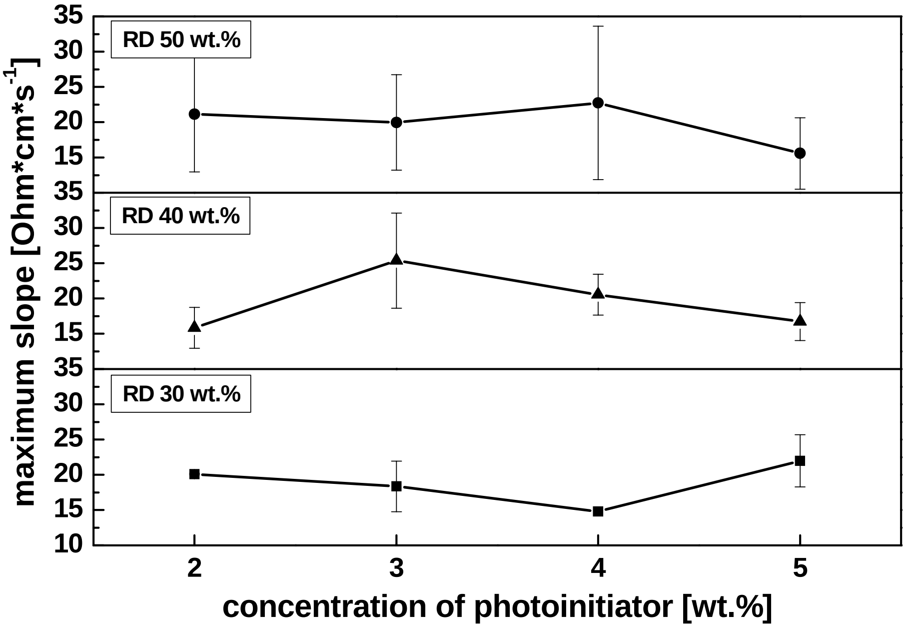


Fig. 2: Maximum slope of the ion viscosity as a function of the photoinitiator concentration (RD: reactive diluent)

Applying photocalorimetry, Scherzer and Decker [27] described an acceleration of the photopolymerization reaction with increasing photoinitiator concentration. This effect is not observable using DEA within the present study. DEA records the curing process on the bottom surface of the 600 µm thick film. High photoinitiator concentrations do not allow for the effective penetration of the UV light in the lower layers. This prevalent filter effect may hinder an acceleration of the cross-linking reaction on the bottom surface.

In Fig. 3 for the different resin formulations the minimum ion viscosity and the maximum ion viscosity at a curing time of 40 seconds are shown dependent on the concentrations of photoinitiator and reactive diluent.

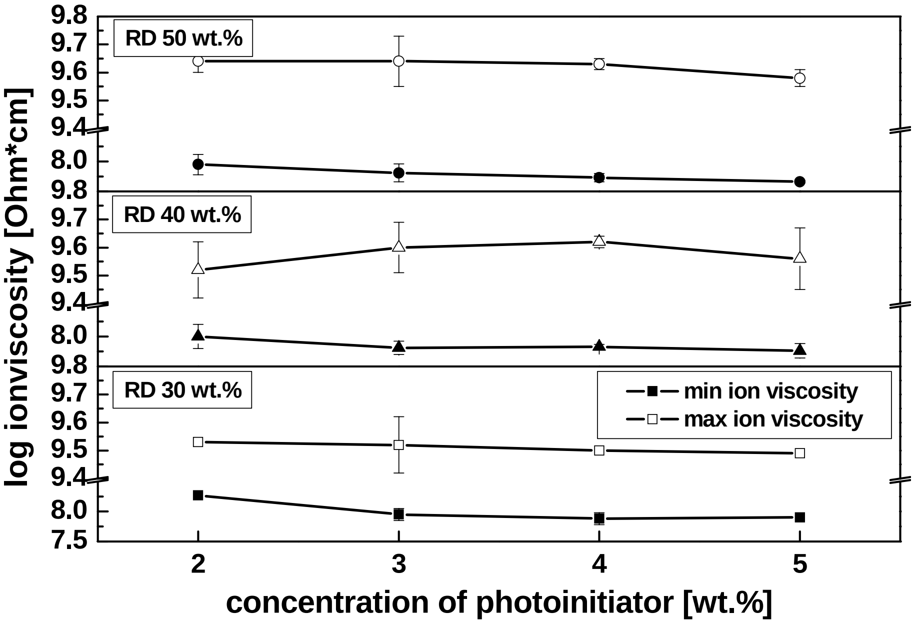


Fig. 3: Minimum and maximum ion viscosity values at a curing time of 40 seconds of the resins determined by DEA as a function of the photoinitiator concentration (RD: reactive diluent)

The minimum ion viscosity decreases with increasing photoinitiator concentration. This enhanced ion conductivity can be ascribed to an augmentation of the concentration of charges with increasing photoinitiator content in the material. Furthermore, a decrease of the minimum ion viscosity with increasing concentration of reactive diluent is discernible. As ion viscosity directly correlates with mechanical viscosity this decrease can be attributed to the thinning effect of the reactive diluent.

The maximum ion viscosity slightly decreases with increasing photoinitiator content. This may again be associated with a change of the conducting ion concentration. Hence, a distinct effect of the photoinitiator content on the maximum ion viscosity is not discernible. This portends similar degrees of conversion for the various resin formulations. Slightly higher maximum ion viscosity values are apparent for resins formulated with higher amounts of reactive diluent. Higher levels of the maximum ion viscosity can be an indication for higher degrees of conversion or be attributable to a change of the resin composition [26]. Thus DEA does not provide detailed information as to the effect of the reactive diluent concentration on the state of cure.

3.2 Attenuated Total Reflectance Spectroscopy (ATR spectroscopy)

In Fig. 4 the degree of conversion on the top surface (surface facing the UV lamp) and the bottom surface (surface facing the dielectric sensor) is plotted as a function of the photoinitiator concentrations for various amounts of reactive diluent added. The bottom surfaces exhibit degrees of conversion between 0.96 and 0.99 with small measurement uncertainties. No effect of the concentrations of photoinitiator and reactive diluent on the degree of cure is observable. This indicates that the higher values of the maximum ion viscosity determined by DEA can be attributed to the change of the resin composition and not to a higher degree of conversion.

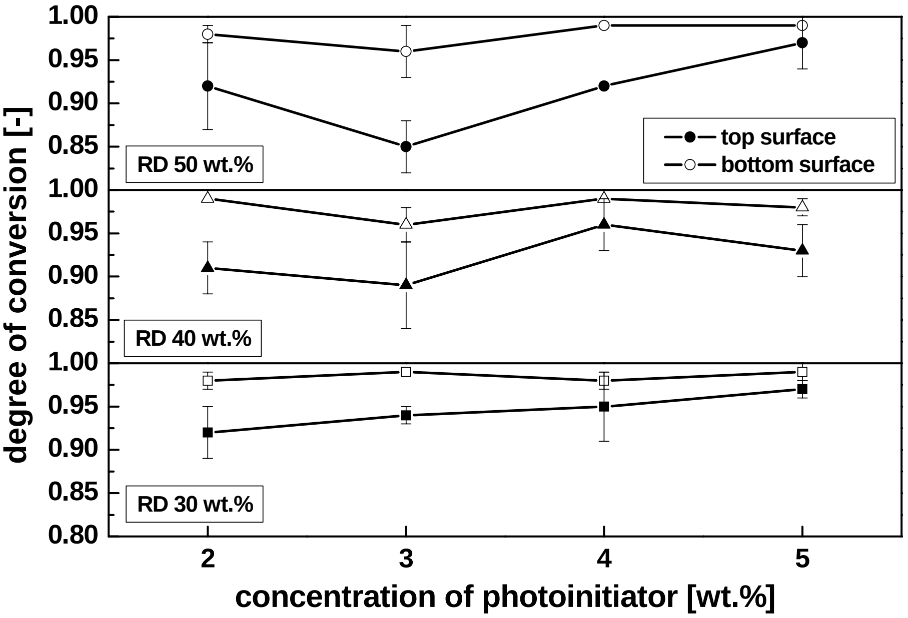


Fig. 4: Degree of conversion on the top surface (surface facing air) and the bottom surface (surface facing dielectric sensor) of the resins determined by ATR spectroscopy as a function of the photoinitiator concentration (RD: reactive diluent)

The top surfaces of the samples show degrees of conversion between 0.85 and 0.96. These lower degrees of cure compared to the bottom surface of the samples and partially undercured states (X<90%), can be attributed to the presence of air during reaction. Atmospheric oxygen makes the monomer conversion less efficient and thus slows down the polymerization reaction [16,17]. From Fig. 4 a tendency is observable that higher photoinitiator concentrations benefit conversion on the films top surfaces. The strong data scatter for the top surface is an indication for locally very different degrees of conversion.

3.3 Dynamic Mechanical Analysis

Figure 6 illustrates the glass transition temperatures of the investigated resin formulations determined by DMA as a function of the photoinitiator concentration for various amounts of reactive diluent added. The resins exhibit glass transition temperatures between 16 and 21°C. No significant differences between the various samples are discernible. The low glass transition temperature is an indication for a high chain mobility and therefore film flexibility. High segment mobility combined with the high molecular weight of the oligomer designates long aliphatic chains and consequently due to the difunctionality a wide meshed network structure in general. Hence, for the investigated resin type the glass transition temperature may not be a sensitive measure for the degree of cure.

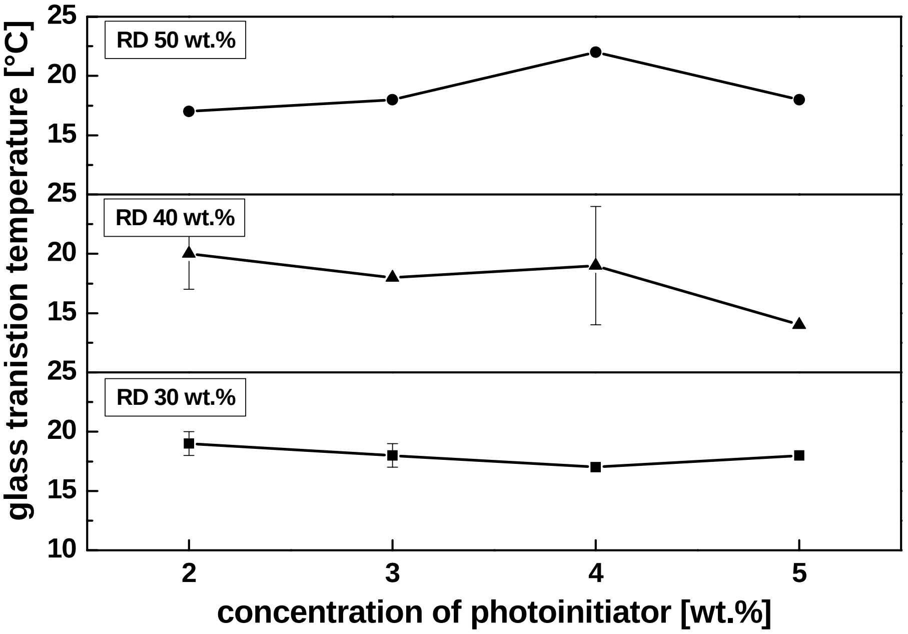


Fig. 5: Glass transition temperature of the resins determined by DMA as a function of the photoinitiator concentration (RD: reactive diluent)

As the curing process and final state of cure of the various resin formulations was ascertained to be independent on the concentrations of reactive diluent and photoinitiator, conclusions as to their suitability for the preparation of thermotropic layers are difficult to draw. In general each of the material formulations can be applied for the production of thermotropic layers. However, it was shown in Resch et al. [18], that the light-shielding performance of thermotropic layers is favored by high glass transition temperatures and cross-linking densities of the resin matrix. Hence, the resins examined within the present study with their high chain mobility and low glass transition temperature are not optimal for the production of thermotropic layers.

4 SUMMARY AND CONCLUSIONS

Within the present investigation the effect of the concentrations of photoinitiator and reactive diluent on the curing characteristics of UV-curable urethane acrylate resins was analyzed applying DEA, ATR spectroscopy and DMA. DEA showed that curing rate and time are independent on the material formulation (measurement uncertainties 0.1 – 25%). Lower sample-lamp distances were found to accelerate the curing process. DEA did not allow for an evaluation of the state of cure as a function of the concentrations of photoinitiator and reactive diluent. ATR spectroscopy revealed that after an irradiation time of 230 seconds for the investigated samples a fully cured state was achieved. No effect of the concentrations of photoinitiator and reactive diluent on the degree of conversion was ascertained. Surface cure was enhanced with higher concentrations of photoinitiator. Regarding the glass transition temperature as a measure for the state of cure, DMA proved similar degrees of conversion of the various resin formulations. The low glass transition temperatures of the samples between 16 and 21°C indicate high chain mobility and flexibility.

5 ACKNOWLEDGEMENTS

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH within the framework of the Non Kplus Program.

This work is funded by the State Government of Styria, Department *Zukunftsfonds Steiermark*.

ZUKUNFTSfonds STEIERMARK   Das Land Steiermark

The authors wish to express their acknowledgements to Cytec Surface Specialties (Drogenbos, BEL) for providing the materials.

References

[1] Meinhardt, S.; Schönfeld, U.; Gödeke, H. Thermo-optical polymer material providing reversible shading DE 4433090 (1996)

[2] Bicer, T.; Gödeke, H.; Werner, J. Method for producing a thermooptical variable polymerized material, and use of same EP 0946443 (1997)

[3] Bicer, T.; Schwitalla, C.; Gödeke, H. Method for producing thermotropic casting resin systems EP 1095080 (1999)

[4] Seeboth, A.; Schneider, J.; Patzak, A. Materials for intelligent sun protecting glazing Solar Energy Materials and Solar Cells 60 (2000), p. 263 - 277

[5] Wilson, H.R. Solar Control Coatings for Windows In Grassie et al. (Eds), Functional Materials – EUROMAT (2000), vol. 13, Wiley, Weinheim, 2000, pp 221 - 233

[6] Schwitalla, C.; Gödeke, H.; König, H. Thermotropic foil and method of manufacturing the same EP 1258504 (2002)

[7] Nitz, P.; Hartwig, H. Solar control with thermotropic layers Solar Energy 79 (2005), p 573 - 582

[8] Resch, K.; Wallner, G.M. Thermotropic resin systems: Relationships between formulation parameters, material structure and optical properties In Proc. Solar World Congress 2007, Beijing, China, pp. 541 - 545

[9] Resch, K.; Wallner, G.M.; Lang, R.W. Spectroscopic investigations of phase- separated thermotropic layers based on UV cured acrylate resins Macromolecular Symposia 265 (2008), p. 49 - 60

[10] Wilson, H.R. Potential of Thermotropic Layers to Prevent Overheating – A Review SPIE 2255 (1994), p. 214 - 225

[11] Raicu, A.; Wilson, H.R. Enhanced energy savings in buildings with thermotropic protection against overheating In Proc. Eurosun 1996, Freiburg, Germany, pp. 1297 - 1302

[12] Khan, A.; Brunger, A. Thermal Protection of Flat Plate Solar Collectors Using Thermotropic Glazings

In Proc. 23rd Annual Conference of the Solar Energy Society of Canada Inc 1997: Implementing Sustainable Energy in a Changing World, Vancouver, Canada, pp. 119 - 124

[13] Granqvist, C.G.; Wittwer, V.
Materials for solar energy conversion: An overview
Solar Energy Materials & Solar Cells 54 (1998), p. 39 - 48

[14] Resch, K.; Hausner, R.; Wallner, G.M.
All Polymeric flat-plate Collector – Potential of Thermotropic Layers to Prevent Overheating
In Proc. Solar World Congress 2007, Beijing, China, pp. 561 - 565

[15] Wallner, G.M.; Resch, K.; Hausner, R.
Property and performance requirements for thermotropic layers to prevent overheating in an all polymeric flat-plate collector
Solar Energy Materials and Solar Cells 92 (2008), p. 614 - 620

[16] Fouassier, J.P.
An introduction to the basic principles in UV curing
In Fouassier and Rabek (Eds) Radiation curing in polymer science and technology, vol. 1, Elsevier London, 1997, pp 49 - 117

[17] Fouassier, J.P.
Photoinitiation, Photopolymerization and Photocuring
Hanser, Munich, 1995

[18] Resch, K.; Wallner, G.M.; Hausner, R.
Phase separated thermotropic layers based on UV cured acrylate resins – structure-property relationships
Submitted to Solar Energy

[19] Kim, B.K.; Lee, K.H.; Kim, H.D.
Preparation and Properties of UV-Curable Polyurethane Acrylates
Journal of Applied Polymer Science 60 (1996), p. 799 - 805

[20] Lecamp, L.; Youssef, B.; Bundel, C.; Lebaudy, P.
Photoinitiated polymerization of a dimethacrylate oligomer: 1. Influence of photoinitiator concentration, temperature and light intensity
Polymer 38 (1997); p. 6089 - 6096

[21] Kim, H.K.; Kim, J.G.; Hong, J.W.
Determination of key variables affecting surface properties of UV curable coatings using experimental design
Polymer Testing 21 (2002); 417 - 424

[22] Rosentritt, M.; Behr, M.; Knappe, S.;
Dielectric Analysis of light-curing dental restorative materials – a pilot study
Journal of Materials Science 41 (2006), p. 2805 –

Handel, G. 2810

[23] Smith, N.T.; O'Malley, T.F. Dielectric Analysis for Determining the Extent of Cure for UV/EB Systems
in Proc. Rad Tech North America 1996
available at Netzsch GmbH, Reprint 113

[24] Rabek, J.F. Experimental and analytical methods for the investigation of radiation curing
In Fouassier and Rabek (Eds) Radiation curing in polymer science and technology, vol. 1, Elsevier London, 1997, pp 239 - 452

[25] Ehrenstein, G.W.; Riedel, G.; Trawiel, P. Praxis der thermischen Analyse von Kunststoffen
Carl Hanser Verlag, Munich, 2003

[26] Stampfer, S.; Ehrenstein, G.W. Dielectric Cure Monitoring of UV-Curing Globe Top Materials for Chip-On-Board Technology
In Proc. SPE ANTEC 1998, Atlanta, USA, p 1173 - 1177

[27] Scherzer, T.; Decker, U. Kinetic investigations on the UV-induced photopolymerization of a diacrylate by time-resolved FTIR spectroscopy: the influence of photoinitiator concentration, light intensity and temperature
Radiation Physics and Chemistry 55 (1999), p. 615 - 619

Keywords:
UV curable acrylates, Dielectric Analysis, Attenuated Total Reflectance Spectroscopy, Dynamic Mechanical Analysis, real-time cure monitoring, degree of cure, cure rate

Stichworte:
UV vernetztende Acrylate, Dielektrische Analyse, Attenuated Total Reflectance Spektroskopie, Dynamisch Mechanische Analyse, Echt-Zeit Erfassung der Vernetzung, Vernetzungsgrad, Vernetzungsgeschwindigkeit

Author/Autor:
Dipl.-Ing. Katharina Resch[1]
Dipl.-Ing. Dr. Gernot M. Wallner[2]
Univ.-Prof. Dipl-Ing. Dr. Reinhold W. Lang[1,2]
(1) Polymer Competence Center Leoben GmbH
Roseggerstrasse 12, 8700 Leoben
(2) University of Leoben
Institute of Materials Science and Testing of Plastics
Franz-Josef Strasse 18, 8700 Leoben

E-Mail: resch@pccl.at
Website: www.pccl.at
Phone.: +43(0)3842/402-2107
Fax: +43(0)3842/402-2102

Please put in long-term contact!

Editor/Herausgeber:
Europe/Europa
Prof. Dr.-Ing. Dr. h.c. G. W. Ehrenstein, verantwortlich
Lehrstuhl für Kunststofftechnik
Universität Erlangen-Nürnberg
Am Weichselgarten 9
91058 Erlangen
Deutschland
Phone: +49/(0)9131/85 - 29703
Fax.: +49/(0)9131/85 - 29709
E-Mail: ehrenstein@lkt.uni-erlangen.de

The Americas/Amerikas
Prof. Dr. Tim A. Osswald,
responsible
Polymer Engineering Center,
Director
University of Wisconsin-Madison
1513 University Avenue
Madison, WI 53706
USA
Phone: +1/608 263 9538
Fax.: +1/608 265 2316
E-Mail: osswald@engr.wisc.edu

Publisher/Verlag:
Carl-Hanser-Verlag
Jürgen Harth
Ltg. Online-Services & E-Commerce,
Fachbuchanzeigen und Elektronische Lizenzen
Kolbergerstrasse 22
81679 Muenchen
Phone.: 089/99 830 - 300
Fax: 089/99 830 - 156
E-mail: harth@hanser.de

4 Performance Properties of Thermotropic Polymer Systems with Fixed Domains

4.1 Introduction

Theoretical modeling demonstrated that thermotropic layers can provide adequate overheating protection for an all-polymeric flat-plate collector with black absorber. It was shown that the solar transmittance of the thermo-functional materials should exceed 85% in clear state to minimize its effect on the overall collector efficiency. To allow for the application of cost efficient plastics as absorber materials the solar transmittance of thermotropic layers needs to be reduced to values below 60% at switching temperatures of 55 to 60°C and 75 to 80°C for thermotropic glazing and thermotropic absorbers, respectively. Furthermore a rapid and steep switching process within a small temperature range is required (Resch et al., 2007; Wallner et al., 2008).

The performance properties of thermotropic layers are affected by morphological parameters. The switching characteristics of a thermotropic material, such as switching temperature and transition temperature range depend on the switching mechanism (i.e. phase separation or change in refractive index of one component) and on the material formulation. In general the light-shielding efficiency is determined by the difference in refractive index between scattering domain and the matrix material as well as by the number of scattering domains, their size and distribution (Wilson, 1994; Nitz, 1999; Goetzberger et al., 2000; Fuchs, 2001; Wilson, 2000; Nitz and Hartwig, 2005). Nitz (1999) performed theoretical modeling to determine scattering domain sizes required for optimum backward scattering of thermotropic materials. The overheating protection performance in the solar spectral range between 250 and 2500 nm was found to be maximized by spherical scattering domains with radii between 100 and 200 nm. This is valid both for a broad range of differences in refractive index of matrix and scattering domains.

According to this the development and systematic optimization of thermotropic materials for overheating protection applications is based on the correlation of performance properties with morphological parameters. In this regard the evaluation requires a comprehensive characterization of

- the solar transmittance in the clear and the opaque state,
- the switching temperature,
- the transition temperature range,
- differences in refractive index between matrix and additive, and
- the scattering domain size and distribution.

Thermotropic hydrogels and thermotropic polymer blends are well examined in the literature as to these parameters (e.g. Beck et al., 1993; Wilson, 1994; Beck et al., 1995; Wilson et al., 1996; Granqvist, 1998; Watanabe, 1998; Georg, 1998; Fuchs, 2001; Raicu et al., 2002). Concerning the development of polymeric thermotropic systems with fixed domains (TSFD) for overheating protection purposes to date 6 patents were published (Dabisch, 1978; Meinhardt et al., 1996; Bicer et al., 1997; Buehler, 1999; Bicer et al., 2000; Schwitalla et al., 2002). However, a comprehensive characterization of their performance properties is not reported yet. Hence, this chapter addresses a comprehensive characterization of TSFD concerning optical and morphological properties. The light-shielding performance is related to morphological parameters. Specific focus is directed towards the demonstration and implementation of an appropriate testing methodology to determine material characteristics which are relevant to control stagnation temperatures in solar collectors.

For the investigations various TSFD are prepared by systematic variation of base resin and additive type. Two different UV-curable matrix materials and five polar and non-polar additive types are chosen. The matrix oligomers include a polyester acrylate (Material A) and a urethane acrylate (Material B). The matrix materials were provided by Cytec Surface Specialties (Drogenbos, BE). As additive types an ester of an alcohol (Additive 1) and paraffin waxes with different melting temperatures (Additives 2 to 5) are considered. The additives were provided by Sasol Germany GmbH (Hamburg, DE) and Chemson Polymer Additive AG (Arnoldstein, AT). The additive concentration is 5 m%.

4.2 Papers 3 and 4

Paper 3: Spectroscopic investigations of phase-separated thermotropic layers based on UV cured acrylate resins
by K. Resch, G.M. Wallner and R.W. Lang
(*Macromolecular Symposia, 265 (2008), 49-60*)

This paper includes a comprehensive characterization of TSFD as to the solar transmittance in the clear and opaque state, the switching temperature and the switching process. Information as to these parameters and aspects is deduced from measurements of the solar transmittance as a function of temperature by UV/Vis/NIR spectroscopy. The implementation of an appropriate measurement device is described. The light-shielding properties of TSFD are related to differences in refractive index between matrix and thermotropic additive, scattering domain size determined by light-microscopy, and scattering particle distribution evaluated by Attenuated Total Reflectance spectroscopy.

Paper 4: Morphology of phase-separated thermotropic layers based on UV cured acrylate resins
by K. Resch and G.M. Wallner
(submitted to: *Polymers for Advanced Technologies*)

This paper includes a comprehensive characterization of TSFD as to additive domain shape and size dependent on material formulation, and the additive domain distribution across the film thickness. Scattering domains are investigated applying high resolution Atomic Force Microscopy in phase imaging mode. Relationships between the scattering domain parameters and the light-shielding efficiency of TSFD are deduced. Furthermore, the effect of additive type on the formation of scattering domains is described.

4.3 Key Literature

Beck, A., Hoffmann, T., Koerner, W., Fricke, J. (1993). Solar Energy **50**, 407.

Beck, A., Koerner, W., Scheller, H., Fricke, J., Platzer, W.J., Wittwer, V. (1995). Solar Energy Materials & Solar Cells **36**, 339.

Bicer, T., Goedeke, H., Werner, J., Schoenfeld, U. (1997). EP 0946443.

Bicer, T., Schwitalla, C., Goedeke, H. (2000). EP 1095080.

Buehler, F. S., Hewel, M. (1999). EP 0985709.

Dabisch, W. (1978). EP 0000868.

Fuchs, K. (2001). „Entwicklung und Charakterisierung thermotroper Polymerblends“, Dissertation, Department of Chemistry and Pharmacy, Albert-Ludwigs-University Freiburg im Breisgau, DE.

Georg, A., Graf, W., Schweiger, D., Wittwer, V., Nitz, P., Wilson, H.R. (1998). Solar Energy **62**, 215.

Goetzberger, A., Mueller, G., Goller, M. (2000). Solar Energy **69**, 45.

Nitz, P. (1999). “Optische Modellierung und Vermessung thermotroper Systeme“, Dissertation, Department of Physics, Albert-Ludwigs-University Freiburg im Breisgau, DE.

Nitz, P., Hartwig, H. (2005). Solar Energy **79**, 573.

Granqvist, C.G., Wittwer, V. (1998). Solar Energy Materials & Solar Cells **54**, 39.

Meinhardt, S., Schoenfeld, U, Goedeke, H. (1996). DE 4433090.

Raicu, A., Wilson, H.R., Nitz, P., Platzer, W., Wittwer, V., Jahns, E. (2002). Solar Energy **72**, 31.

Resch, K., Hausner, R., Wallner, G.M. (2007). In Proc. Solar World Congress 2007, pp. 561-565, September 18-21, Beijing, CN.

Schwitalla, C., Goedeke, H., Koenig, H. (2002). EP 1258504.

Wallner, G.M., Resch, K., Hausner, R. (2008). Solar Energy Materials and Solar Cells **92**, 614.

Watanabe, H. (1998). Solar Energy Materials & Solar Cells **54**, 203.

Wilson, H. R. (1994). SPIE; Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XIII **2255**, 214.

Wilson, H.R., Raicu, A., Nitz, P. (1996). In Proc. Eurosun 1996, pp. 534-539, September 16-19, Freiburg, DE.

Wilson, H.R. (2000). Functional Materials – EUROMAT 99 **13**, 221.

Macromol. Symp. **2008**, 265, 49–60 DOI: 10.1002/masy.200850506

Spectroscopic Investigations of Phase-Separated Thermotropic Layers Based on UV Cured Acrylate Resins

Katharina Resch,[*1] *Gernot M. Wallner,*[2] *Reinhold W. Lang*[1,2]

Summary: In this paper spectroscopic techniques were adapted and applied to characterize the optical and morphological properties of thermotropic resins. Thermotropic films were prepared by variation of resin base and thermotropic additives. By UV/Vis/NIR spectroscopy the solar optical properties, the switching temperature, the switching process and the residual transmittance in the opaque state were determined. To control the sample temperature from ambient to 100 °C a conventional UV/Vis/NIR spectrophotometer equipped with an Ulbricht-sphere was adapted by a heating stage. Additive content, distribution and scattering domain size were characterized by Differential Scanning Calorimetry, Attenuated Total Reflectance spectroscopy and microscopic techniques. For the investigated film types hemispheric solar transmittance values ranging from 80 to 87% and 75 to 85% were obtained in the clear and the scattering state, respectively. The diffuse solar transmittance values increased significantly from 14 to 40% below the switching temperature to 36 to 70% at elevated temperatures. The thermotropic resins exhibit a steep and rapid switching process with switching temperatures between 45 and 70 °C. The materials with the best switching properties are characterized by distinct differences in refractive index between the components, a uniform additive distribution and scattering domains with diameters below 1000 nm.

Keywords: infrared spectroscopy; overheating protection; refractive index; thermotropic resins; UV-Vis spectroscopy

Introduction

Polymeric materials are playing a key-role in the future development of solar energy systems, as they offer significant potential for cost savings in solar thermal collectors and may thus benefit a broader utilization of solar energy, specifically for low-temperature heating purposes. Especially for domestic hot water generation and space heating applications, where the required maximum operating temperature of the absorber is about 80 °C, cost-efficient plastics will be applied. However, conventional solar thermal collectors reach stagnation temperatures up to 200 °C, which exceed the maximum operating temperatures of cost-efficient plastics (~80–140 °C). Absorbers made of such plastics tend towards irreversible deformation and/or degradation when exposed to elevated temperatures of 200 °C for prolonged periods. Therefore an appropriate overheating protection is required. The energy flux in an all-polymeric flat-plate collector can be controlled by thermotropic layers.[1,2] Thermotropic materials change their light transmission behavior from highly transparent to light diffusing upon reaching a certain threshold temperature.[3,4] Thus such actively switchable layers permit the light and energy flux to be adapted dynamically to climatic

---

[1] Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria
Fax: (+43) 3842 402 2102;
E-mail: resch@pccl.at

[2] Institute of Materials Science and Testing of Plastics, University of Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria

demands. By theoretical modeling of an all-polymeric flat plate collector it was found that for adequate overheating protection (i.e. stagnation temperatures ranging from 80 to 140 °C) switching temperatures between 55 and 60 °C as well as a residual hemispheric solar transmittance of 25 to 60% in the opaque state are effectual.[1]

In thermotropic materials that undergo a transition from transparent to light diffusing, the light is scattered from particles, which exhibit an index of refraction, which is different to that of the matrix.[3,4] In the past various thermotropic systems for active daylight control in transparent facades have been developed and investigated.[3–10] Whereas in thermotropic polymer blends and hydrogels the switching is involved in a phase separation, in thermotropic resins, the scattering domains are embedded statically in a matrix material.[3] To the best of our knowledge, comprehensive and systematic development and research on thermotropic materials for solar thermal systems has not yet been performed. Hence, the overall objective of our research is to perform a comprehensive development and characterization of thermotropic materials for overheating protection of solar collectors and to establish structure-property relationships. Various thermotropic resins were manufactured by systematic variation of base resin formulation as well as of additive type. The materials are characterized as to their optical properties and switching characteristics on a UV/Vis/NIR spectrophotometer equipped with an Ulbricht-sphere to differentiate between diffuse and direct transmitted light. Additionally the indices of refraction are considered. Scattering domain size, additive content and distribution of the thermotropic resins are characterized applying Differential Scanning Calorimetry, light microscopy and Attenuated Total Reflectance spectroscopy.

Material Preparation

Thermotropic layers were prepared by dissolving the thermotropic additives in a photo-crosslinkable matrix solution, which consists of oligomers, a reactive diluent as well as a photoinitiator. For the present study 2 different oligomer systems (oligomers A and B) serving as the main component of the matrix material were selected. In order to meet the requirements as to overheating protection of solar thermal systems, 3 thermotropic additives exhibiting switching temperatures of 47, 54 and 60 °C were selected (additive types 1, 2 and 3).[1] The additive concentration chosen for the preparation of the films was 5 wt%. The dissolution of the thermotropic additive in the resins was filled into an intervening space located between two glass panes, which were sealed around the edge. Afterwards the mixture was cured by UV-radiation (Ultra Vitalux, Osram GmbH, München, GER) for 5 minutes. The film thickness was 800 μm. As to the nomenclature A-1 indicates a film based on resin A containing additive type 1, for example.

Characterization of Optical Properties

The refractive indices of the additives and the resins were determined on a m-line apparatus (Metricon model 2010 (Metricon Corp., Pennington, USA)) based on the prism coupling technique. All measurements were performed at temperatures from 25 to 100 °C using a He-Ne laser with a wavelength of 633 nm.

The thermotropic materials were analyzed as to solar transmittance values in clear and opaque state, switching temperature and switching process applying UV/Vis/NIR spectroscopy. Hemispheric and diffuse transmittance spectra were recorded at normal incidence within a wavelength range between 250 and 2500 nm on a conventional UV/Vis/NIR spectrophotometer (Lambda 950, Perkin Elmer Instruments GmbH, Überlingen, GER) equipped with an Ulbricht-sphere (diameter 150 mm). For the given measurement apparatus the radiation passing through the specimen outside a cone of approximately 5° relative to the incident beam direction is defined as diffuse (scattered) component.

The measured spectral data were weighted in steps of 5 nm by the AM 1.5 global solar irradiance source function, given in Bird and Hulstrom[11] and representing the spectral distribution of solar radiation energy, when the sun is at approximately 42° above the horizon at sea level where the solar radiation has traveled 1.5 atmospheres. By this way integral solar transmittance values were determined.

To investigate the switching behavior (i.e. switching characteristic and temperature) the spectrophotometer was adapted by a heating stage allowing for controlling the sample temperature from ambient to 100 °C. For the determination of films thermal transitions the samples were mounted in a heating-chamber within the standard sample chamber of the spectrophotometer using a purpose-built clamp. This clamp has been additionally adapted by sensors to acquire the temperatures of the chamber and the sample. Due to this setup the sample is not positioned directly at the entrance of the integrating sphere. Especially for highly diffuse scattering samples this causes significant chamber recess error, which in turn results in considerable deviations between the recorded values and the effective radiation transmitted by the sample. To avoid these radiative losses on the one hand the inner boundaries of the light transmitting recess in the heating chamber were covered with a highly reflective mirror film which exhibits direct-direct and direct-diffuse solar reflectance values of 80 and 5%, respectively. On the other hand, the dimension of the incident light beam striking the sample has been reduced by a pinhole that was mounted at the front side of the heating chamber. With this configuration even for highly diffuse scattering samples more accurate transmittance values were measured. However, slight differences between the detected values and the effective radiation transport were obtained, which can be attributed to absorption of the mirror film (merely 85% solar reflectance). Thus a calibration of the recorded data is required. For this purpose hemispheric and diffuse transmittance spectra of numerous weak and highly scattering samples were recorded both by positioning the samples direct within the portholes of the Ulbricht-sphere and by mounting the materials in the adapted heating stage. In Figure 1 hemispheric and diffuse solar transmittance values, recorded at the different sample positions are compared. Excellent linear correlations with regression coefficients of 0.99 and 0.96 for hemispheric and diffuse solar transmittance values, respectively,

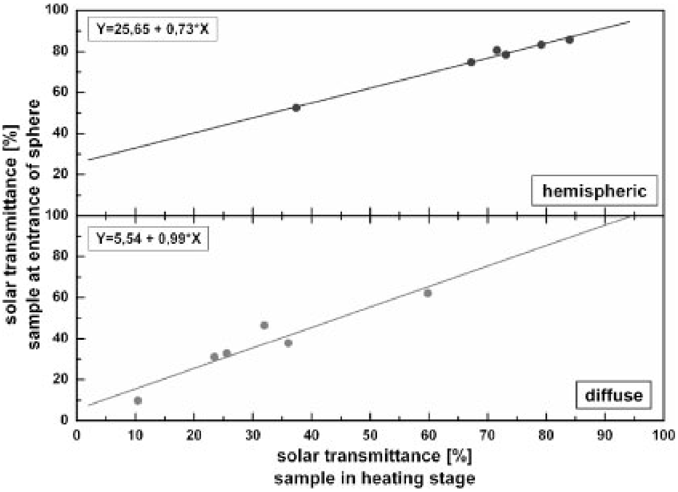


Figure 1.
Calibration for hemispheric and diffuse transmittance.

were obtained. All data presented in the following have been corrected by the corresponding equations of the linear regressions given in Figure 1.

Transmittance measurements were performed in steps of 5 K. Prior to the measurements the sample was maintained at the selected temperature for 10 minutes.

Characterization of Morphology

The additive contents of the produced thermotropic layers were determined by Differential Scanning Calorimetry operating in Temperature Modulation mode (TM-DSC). TM-DSC was performed under static air from 0 °C to 130 °C at a heating rate of 1 K/min, a modulation amplitude of ±0.5 °C and a modulation period of 75 s on a Mettler Toledo DSC822e (Schwarzenbach, CH). Weighting the transition enthalpy of the thermotropic layer by the heat of fusion of the pure additive allowed for the evaluation of the films additive content.

To obtain information as to film composition and additive distribution on the surface of the thermotropic materials Fourier Transform Infrared (FT-IR)-spectroscopy was performed in Attenuated Total Reflection mode (ATR) within a wavenumber range from 700 to 4000 cm^{-1} at a resolution of 1 cm^{-1} using a diamond crystal (Spectrum One, Perkin Elmer Instruments GmbH, Überlingen, GER). The recorded spectra were corrected for the wavelength-dependent penetration depth of the evanescent wave as well as for the baseline by the *Spectrum v. 5.0* software (Perkin Elmer Instruments GmbH, Überlingen, GER).

Additive particle sizes were characterized applying optical microscopy. Transmitted light micrographs were recorded on an Olympus BX51 (Olympus GmbH, Hamburg, GER) microscope at a magnification of 50×.

Results and Discussion

In Figure 2 a representative thermotropic resin (layer A-1) in transparent and light diffusing state is depicted. The thermotropic material is perfectly clear below the switching temperature (left side). At elevated temperatures the light scattering of the sample increases, which causes the material to turn opaque.

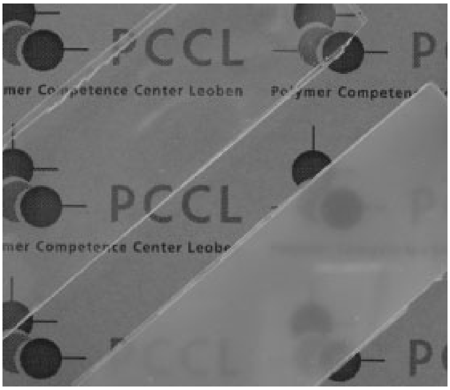


Figure 2.
Thermotropic layer A-1 in clear (left) and scattering state (right).

In Figure 3 to 6 hemispheric and diffuse transmittance spectra of the different thermotropic layers based on the resins A and B in the clear and scattering state are depicted, respectively. In the transparent state (solid line) all layers show a hemispheric transmittance of about 80% in the visible and the near-infrared region (Figure 5 and 7). No significant differences between the various materials are apparent. Interactions between the films and the solar radiation which reduce transmission occur below 380 and above 1200 nm. Below 380 nm the transmittance decreases due to absorption of incorporated ultraviolet absorbers. Absorption bands at approximately 1200, 1400 and 1700 nm and above 2225 nm can be attributed to vibrations of carbon-hydrogen single bonds (C–H). The peak at 2150 nm appears due to stretching of carbon-oxygen double bonds in the polymers (C=O). The absorption peak at about 1900 nm refers to water molecules absorbed by the material. In the scattering state (dotted line) material B-1 displays slightly higher transmittance values compared to the clear state. For the other layers

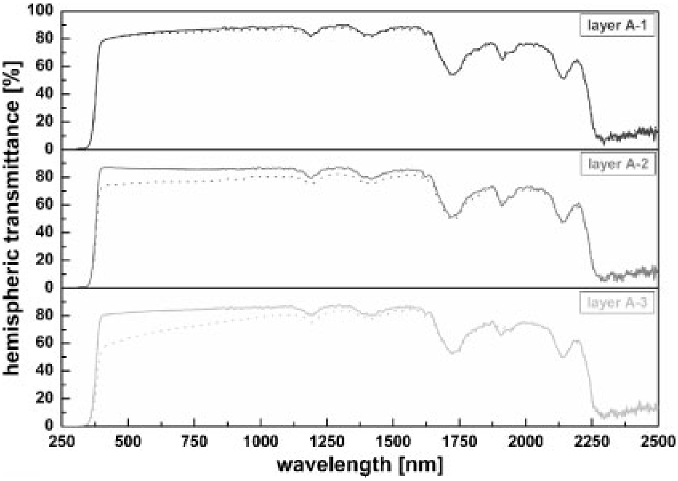


Figure 3.
Hemispheric transmittance spectra of thermotropic layers based on resin A in clear and scattering state; top: layer A-1; mid: layer A-2 and bottom: layer A-3 (solid line: clear state; dotted line: scattering state).

a decrease of the hemispheric transmission is discernible at elevated temperatures. In general these layers show a stronger decrease of transmission in the region between 300 and 1500 nm than at longer wavelengths. The differences in transmission between the clear and the scattering state increase with decreasing wavelength. The reduction of transmittance is more pronounced for materials A-2, A-3 and B-3. This indicates that these layers exhibit better light shielding properties than film types A-1, B-1 and B-2.

The diffuse transmittance spectra of the investigated thermotropic materials shown in Figure 4 and 6 give information as to their scattering properties. The spectra reveal significant differences in the film's scattering behavior. All film types exhibit an increase of diffuse transmittance with

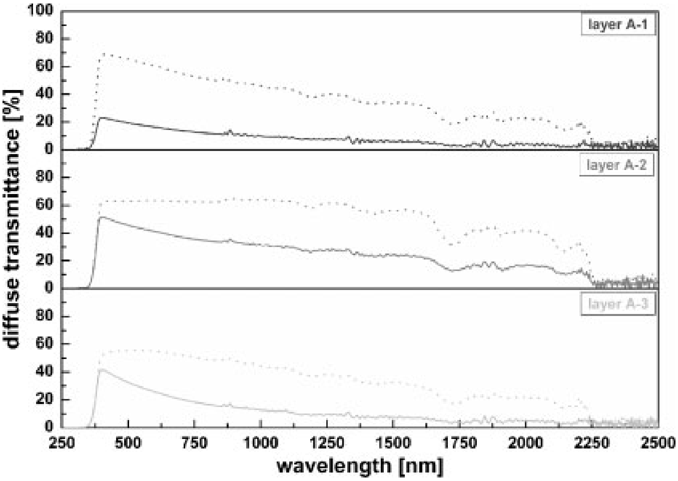


Figure 4.
Diffuse transmittance spectra of thermotropic layers based on resin A in clear and scattering state; top: layer A-1; mid: layer A-2 and bottom: layer A-3 (solid line: clear state; dotted line: scattering state).

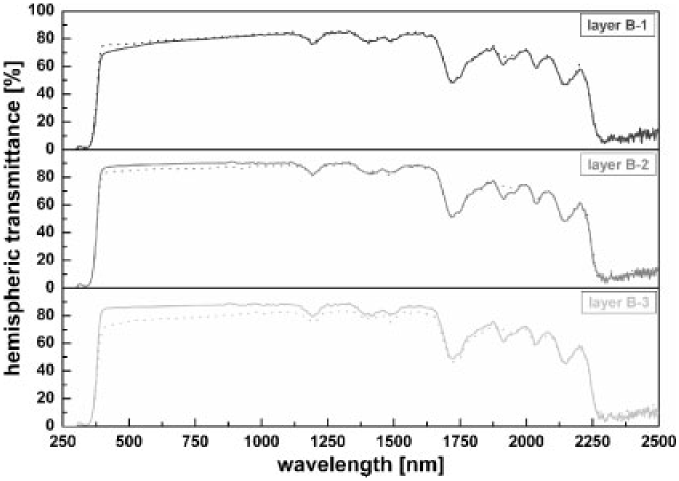


Figure 5.
Hemispheric transmittance spectra of thermotropic layers based on resin B in clear and scattering state; top: layer B-1; mid: layer B-2 and bottom: layer B-3 (solid line: clear state; dotted line: scattering state).

decreasing wavelength. Whereas additive type 1 yields lower diffuse scattering for layers based on resin A, additives types 2 and 3 reduce the diffuse scattering power for layers produced on the basis of resin B in the clear state (solid line). For the films A-1, B-2 and B-3 the diffuse transmittance values were found to remain below 30% over the whole wavelength range only slightly increasing with decreasing wavelength. For the layers A-2, A-3 and B-1 a more pronounced increase of the diffuse transmittance values in the short wavelength range was observed associated with also higher diffuse transmittance values in the near infrared wavelength range. In the scattering state (dotted line) a significant increase of diffuse transmittance is discernible in the wavelength range between 380 and 2250 nm. The most pronounced rise

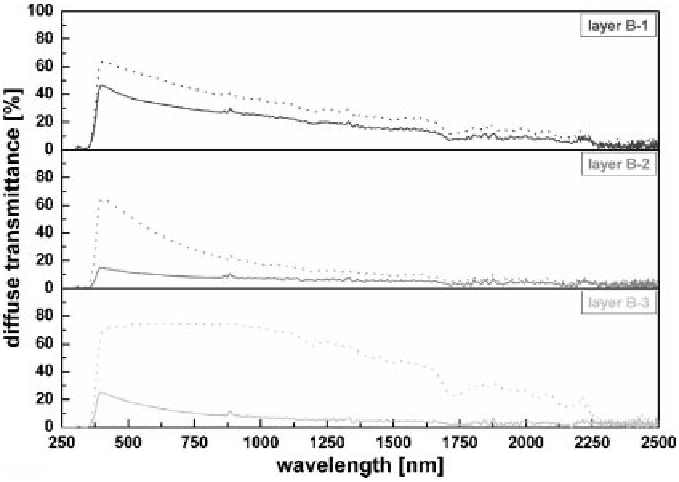


Figure 6.
Diffuse transmittance spectra of thermotropic layers based on resin B in clear and scattering state; top: layer B-1; mid: layer B-2 and bottom: layer B-3 (solid line: clear state; dotted line: scattering state).

of diffuse scattering power was found for the layers A-1 and B-3. Layer B-1 exhibits the less distinct changes. The differences in diffuse scattering below and above the switching temperature increase with decreasing wavelength for layers A-1, B-1 and B-2. For the layers showing the most significant reduction of hemispheric transmittance (layers A-2, A-3, B-3) this tendency is not observable.

The hemispheric and diffuse transmittance spectra of the samples clearly indicate that the thermotropic layers undergo a transition from a clear to a scattering state. Accurate relationships between material formulation and the scattering behavior may be emphasized by integral solar optical properties determined over the solar spectral intensity AM 1.5. Thus in Table 1 integral solar optical properties (hemispheric and diffuse transmittance) of the investigated thermotropic layers in the clear and the opaque state are summarized. Below the switching temperature all samples exhibit an excellent hemispheric transmittance above 80%. For the diffuse transmittance considerable differences between the various material formulations are observable. The values range from 14 to 40%. Whereas for layers based on resin A additive type 1 yields lower diffuse scattering, materials with resin B matrix show better optical properties with the additive types 2 and 3. In the scattering state at elevated temperatures the diffuse transmittance increases significantly to values exceeding 36%. The most distinct changes are observable for the layers B-3 and A-1, where the forward scattered light increases by 53 and 37%. The diffuse transmittance of the other layers increases by 13 to 26%. Already a change of the diffuse transmittance of 13% is associated by a loss of view-through behavior. However, the overheating protection properties are determined by the reduction of hemispheric transmittance. The hemispheric transmission of the films is decreased above the switching temperature to a smaller extent. The most significant changes were found for thermotropic layers being formulated with additive type 3. By dispersing this additive type in the resins A and B the hemispheric transmittance is reduced by 6 and 9%, respectively. A reasonable decrease of the hemispheric transmission was also obtained for material A-2 (6%). For material B-1 an increase of transmittance from 80 to 81% is discernible. This layer exhibits a significant increase of transmittance to values of 85% at temperatures between 30 and 45 °C.

To describe the switching characteristics of the materials in Figure 7 and 8 the diffuse solar transmittance is plotted as a function of temperature for thermotropic materials based on resin A and B, respectively. For thermotropic layers being formulated with additives 1 and 2 the switching gradient is reasonably steep, so that the diffuse solar transmittance changes within a small temperature range of 10 to 15 K. The temperature at which this transition occurs (switching temperature) ranges between 40 and 50 °C for these film types. Whereas for the thermotropic layer produced from

Table 1.
Hemispheric and diffuse solar transmittance values of the thermotropic layers in clear and scattering state.

Resin	Additive type	Solar transmittance			
		Clear state		Scattering state	
		Hemispheric [%]	Diffuse [%]	Hemispheric [%]	Diffuse [%]
A	1	85	19	84	56
	2	85	40	79	64
	3	84	25	75	51
B	1	80	34	81	47
	2	87	14	85	36
	3	86	17	80	70

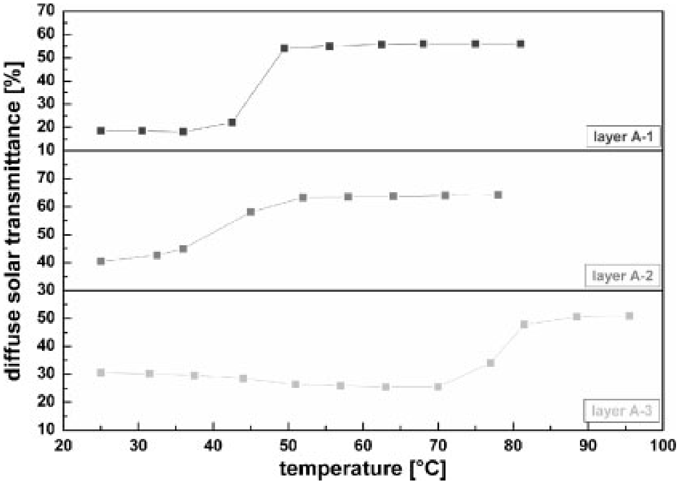


Figure 7.
Diffuse solar transmittance of thermotropic layers based on resin A as a function of temperature; top: layer A-1; mid: layer A-2 and bottom: layer A-3.

additive type 3 and resin B the switching again proceeds at a temperature of about 45 °C, the transition from the clear to the scattering state is more gradual. In contrast the thermotropic layer produced from resin A and additive type 3 shows a very steep switching process. However, the switching temperature of this film is shifted to above 70 °C.

Both, the scattering spectra and the solar optical transmittance data presented in Table 1 reveal significant differences in the scattering behavior between the various thermotropic layers. In general the optical properties and the switching behavior of the thermotropic materials are determined both, by the differences in refractive index between the additives and the matrix

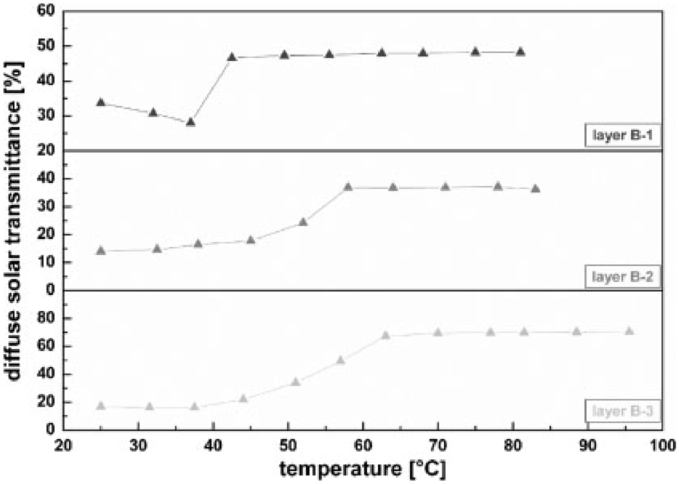


Figure 8.
Diffuse solar transmittance of thermotropic layers based on resin B as a function of temperature; top: layer B-1; mid: layer B-2 and bottom: layer B-3.

material below and above the switching temperature, and by the scattering domain size and number of scattering particles, which is correlated to additive content.[12] The consideration of these parameters is of significant importance for the establishment of a fundamental understanding of the layers switching characteristics and a systematic material development and optimization.

In Figure 9 the refractive indices of the additives and the matrix materials are compared at different temperatures. For the resins A and B refractive indices of 1.52 and 1.50 were determined at low temperatures, respectively. The insignificant decrease of 1.1 (resin A) and 1.3% (resin B) in the temperature range between 25 and 95 °C indicates that the refractive index of the resins is not affected by changes in temperature. The refractive index of additive type 1 switches steeply from 1.52 to 1.45 within 40 and 50 °C. For additive type 2 the refractive index decreases from 1.50 to 1.42 in the temperature range from 25 to 50 °C. For additive type 3 the decrease of the refractive index is more gradual. It changes from 1.52 to 1.43 in a temperature range between 30 and 90 °C.

In general below the switching temperature a reasonable match of the refractive indices of the resins and the thermotropic additives with differences between 0 and 0.02 was detected. Whereas hemispheric transmittance values were found to be insignificantly affected by the differences in the refractive index of the components, the diffuse transmittance varies between the different film types. An increasing diffuse transmittance with increasing difference in refractive index is observable. Figure 9 shows that the differences in the refractive indices of the components at elevated temperatures are more pronounced for the additive types 2 and 3 compared to additive type 1. This may be attributed to a more distinct change in the refractive index of the additive types 2 and 3. However, at elevated temperatures no correlations between the differences in refractive index and the scattering properties of the samples are observable. This indicates that the optical properties of the considered thermotropic layers are further dependent on the additive concentration and distribution as well as on scattering domain size.

As to additive content significant deviations from the theoretical concentration were ascertained, especially for the resins formulated with additive types 2 and 3. For additive type 2 dispersed in the resins A and

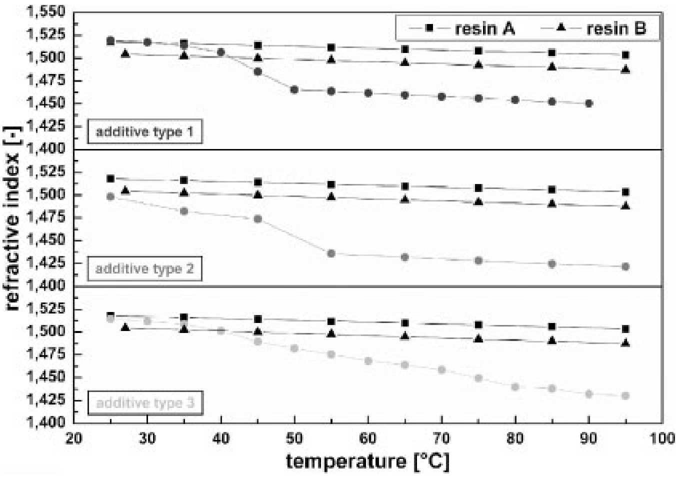


Figure 9.
Refractive indices of resins A and B and the thermotropic additives at a wavelength of 633 nm as a function of temperature; top: resins vs. additive type 1, mid: resins vs. additive type 2 and bottom: resins vs. additive type 3.

B the additive content amounts to 1.33 and 1.60 wt.%, respectively. Scattering domain concentration in films formulated with additive type 3 is even lower with 0.95 and 1.09 wt.% for layers based on resin A and B. The highest additive content was found for thermotropic materials containing additive type 1 with values of 3.87 and 4.80 wt.% in layers A-1 and B-1.

In Figure 10 and 11 ATR spectra in the wavenumber range from 3050 to 2800 cm^{-1} of the various thermotropic layers and the neat resins are depicted. For the thermotropic materials spectra are shown both, for the front side, i.e. the side faced to the UV light source during the curing and for the opposite side, i.e. the back side of the films. Information as to additive concentration on the surface can be deduced from the decrease of transmission at wavenumbers of 2848 and 2915 cm^{-1}, which can be attributed to symmetric and asymmetric stretching vibrations of methylene groups ($–CH_2–$), respectively. In general the absorption bands are more pronounced for thermotropic layers produced from additive type 1 than for materials formulated with the additive types 2 and 3. This can be ascribed to the higher additive concentration of layers containing additive type 1. Whereas for thermotropic materials based on the additive types 2 and 3 no differences between the two film sides are observable, additive concentration is higher on the front surfaces of layers formulated with additive type 1. It is observable that the absorption peaks are more distinct for thermotropic materials based on resin B. On the one hand this can be attributed to the slightly higher additive content of these materials. On the other hand it may be an indication for a less uniform additive distribution across the film thickness.

The scattering domain sizes of the thermotropic layers were determined applying light microscopy. For materials based on resin A and formulated with the additive types 1, 2 and 3 average particle diameters of 1.7, 1.0 and 0.8 μm were obtained, respectively. Thermotropic layers based on resin B and formulated with additive types 1, 2 and 3 exhibit scattering domains with diameters of 1.4, 2.2 and 1.1 μm, respectively. In

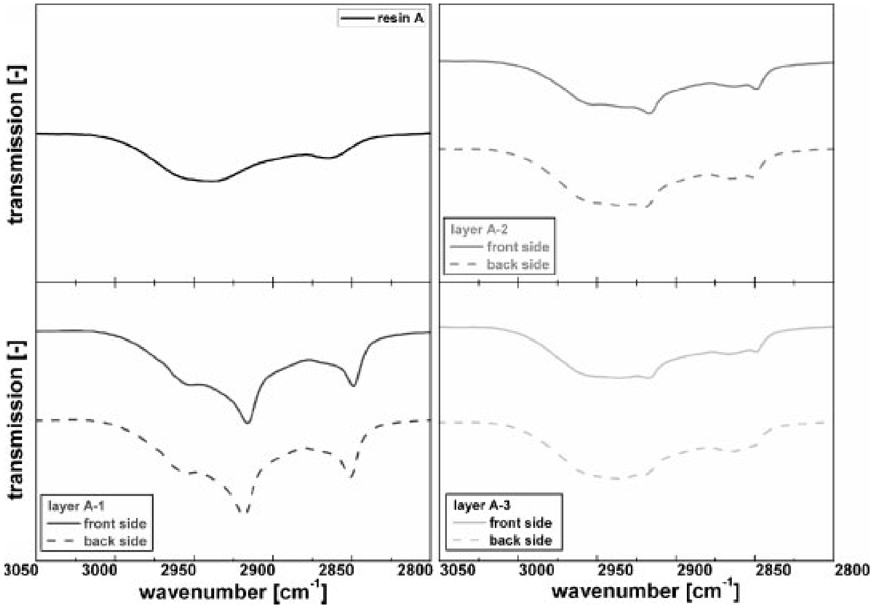


Figure 10.
ATR spectra of resin A and the thermotropic layers based on resin A in the wavenumber range between 3050 and 2800 cm^{-1}; top left: resin A, bottom left: layer A-1, top right: layer A-2 and bottom right: layer A-3.

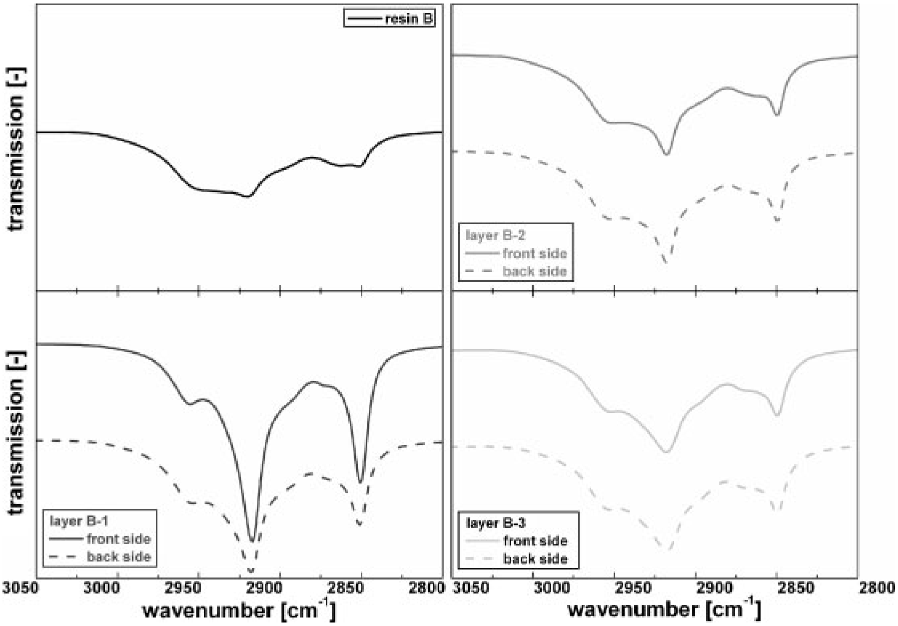


Figure 11.
ATR spectra of resin B and the thermotropic layers based on resin B in the wavenumber range between 3050 and 2800 cm^{-1}; top left: resin B, bottom left: layer B-1, top right: layer B-2 and bottom right: layer B-3.

general a tendency was observed that with decreasing particle sizes the light shielding properties of the thermotropic layers are enhanced. Nevertheless, for maximum reflectance efficiency in the solar wavelength range scattering radii of 100 to 200 nm are required.[5,6,12,13] The scattering domain sizes of the thermotropic materials produced within the present study are significantly larger, which results in less light-shielding capability.

Furthermore the micrographs of the materials depicted a higher aggregation of additives for materials based on resin B. This is convenient with ATR spectra, revealing higher additive concentrations on the surface for these materials. For layer B-3 the additives are less pronounced on the surfaces. Because light microscopy does not allow for a detailed analysis of scattering domain size distribution further investigations are currently carried out using Atomic Force Microscopy (AFM).

As to the influence of morphological parameters on the optical properties of the films it was found that although additive concentration is higher for thermotropic layers based on resin B, both the forward and the back scattering power above the switching temperature is higher for materials produced from resin A. This may be ascribed to the more uniform additive distribution across the film thickness for these materials. The decreased hemispheric solar transmittance of the layers A-1, A-2 and B-3 above the switching temperature can be attributed to the smaller scattering domain size of these films. In general a tendency is observable that decreasing scattering domain size increases the diffuse scattering power. Furthermore a more uniform distribution of the additives across the film thickness yields better light-shielding properties, and thus higher opacity in the scattering state.

Summary and Conclusion

In this paper the optical and morphological properties of thermotropic resin materials are described and discussed. In the clear state the investigated films exhibit direct-hemispheric solar transmittance values of 80 to 87%, with diffuse fractions ranging from 14 to 40%. The materials undergo a transition from the clear to the scattering state at temperatures between 40 and 75 °C. The investigated thermotropic resins exhibit a steep and rapid switching process. Above the switching temperatures the hemispheric solar transmission decreases to values between 75 to 85%, with diffuse fractions ranging from 36 to 70%. The materials show a stronger decrease of transmittance in the visible than in the near infrared region.

The optical properties of the films in the clear and the scattering state were found to be significantly dependent on the differences in the refractive indices of the components, additive content and distribution as well as on scattering domain size. The light-shielding properties of the thermotropic layers and thus the opacity in the opaque state are enhanced by more pronounced differences in refractive index between matrix and additive (>0.04), a uniform additive distribution across the film thickness and scattering particles with dimensions below 1000 nm.

Acknowledgements: The research work of this paper was performed at the Polymer Competence Center Leoben GmbH within the framework of the K_{plus} Program of the Austrian Ministry of Traffic, Innovation and Technology with the contributions by the University of Leoben, Graz University of Technology, Johannes Kepler University Linz, JOANNEUM RESEARCH Forschungsgesellschaft mbH and Upper Austrian Research GmbH. The PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

This work is funded by the State Government of Styria, Department *Zukunftsfonds Steiermark*.

The authors wish to express their acknowledgements to Cytec Surface Specialties (Drogenbos, BEL), Sasol Germany GmbH (Hamburg, GER) and Chemson Polymer Additive AG (Arnoldstein, AUT), for providing the materials.

[1] K. Resch, R. Hauner, G. M. Wallner, in *"Proceedings of ISES SWC 2007"*, September 18–21 2007, in press.

[2] G. M. Wallner, K. Resch, R. Hausner, in *"Proceedings of Gleisdorf Solar 2006"*, September 6–8 2006, p. 105ff.

[3] A. Seeboth, J. Schneider, A. Patzak, *Solar Energy Materials and Solar Cells* **2000**, *60*, 263.

[4] P. Nitz, H. Hartwig, *Solar Energy* **2005**, *79*, 573.

[5] A. Beck, T. Hoffmann, W. Körner, J. Fricke, *Solar Energy* **1993**, *50*, 407.

[6] A. Beck, W. Körner, H. Scheller, J. Fricke, W. J. Platzer, V. Wittwer, *Solar Energy Materials and Solar Cells* **1995**, *36*, 339.

[7] H. Watanabe, *Solar Energy Materials and Solar Cells* **1998**, *54*, 204.

[8] A. Georg, W. Graf, D. Schweiger, V. Wittwer, P. Nitz, H. R. Wilson, *Solar Energy* **1998**, *62*, 215.

[9] J. Schneider, A. Seeboth, *Materialwissenschaft und Werkstofftechnik* **2001**, *32*, 231.

[10] A. Raicu, H. R. Wilson, P. Nitz, W. Platzer, V. Wittwer, E. Jahns, *Solar Energy* **2002**, *72*, 31.

[11] R. E. Bird, R. L. Hulstrom, *Solar Energy* **1983**, *30*, 563.

[12] P. Nitz, *"Optische Modellierung und Vermessung thermotroper Systeme"*, 1999, Ph.D. Thesis, Albert- Ludwigs-Universität in Freiburg im Breisgau, Germany.

[13] C. G. Granqvist, V. Wittwer, *Solar Energy Materials and Solar Cells* **1998**, *54*, 39.

Morphology of phase-separated thermotropic layers based on UV cured acrylate resins

Katharina Resch[1), Gernot M. Wallner[2)

[1) Polymer Competence Center Leoben GmbH
Roseggerstrasse 12, 8700 Leoben, Austria

[2) Institute of Materials Science and Testing of Plastics, University of Leoben
Franz-Josef Strasse 18, 8700 Leoben, Austria

Abstract

Within this paper, relationships between the scattering domain parameters (size and shape) and the light-shielding properties of thermotropic systems with fixed domains are established. Specific focus is given to the effect of additive type on the formation of scattering domain size. Various functional layers are prepared by a variation of thermotropic additives. Scattering domains are investigated applying high resolution Atomic Force Microscopy in phase imaging mode. Thermotropic layers formulated with additive types exhibiting a short chain length display roughly spherical scattering particles with dimensions between 0.5 and 3 µm and a moderate reduction in hemispheric solar transmittance along with a significant increase of diffuse solar transmittance above the switching threshold. Additive types with long-chain molecules develop anisotropic scattering domains resembling distorted disks with a diameter up to 50 µm and a thickness between 100 and 400 nm. Disk-like scattering features yield enhanced light-shielding properties.

Keywords: thermotropic systems with fixed domains, Atomic Force Microscopy, scattering domain size, light-shielding efficiency

1. Introduction

Thermotropic glazings reversibly change their light transmittance upon reaching a certain threshold temperature (Seeboth et al, 2000; Nitz, 2005; Resch, 2008b). Materials types that show a transition from a transparent to an opaque state can prevent overheating in solar thermal systems (Wallner et al., 2008). Recent publications deal with thermotropic systems with fixed domains (TSFD), that consist of a thermotropic additive dispersed in a resin matrix, for overheating protection purposes in solar collectors (Resch and Wallner, 2007; Resch et al., 2008a; Resch et al. 2008b; Resch et al. 2008c). Spectroscopic investigations as to optical and morphological properties revealed a reduction of the hemispheric solar transmittance by maximum 18% (Resch et al., 2008a; Resch et al., 2008b). As shown by Wallner et al. (2008) for a collector with twin-wall sheet glazing and black absorber a reduction of the solar transmittance by at least 25% is required to limit stagnation temperatures to values below 130°C and accordingly to allow for the application of cost-efficient plastics as absorber materials. Hence, to prevent overheating in solar collectors, the light-shielding performance of the considered TSFD has to be improved. The back scattering efficiency is mainly affected by the scattering domain size, which should range between 200 and 400 nm in diameter (Nitz, 1999; Nitz and Wilson, 2008). Material development concerning TSFD so far did not consider relationships between morphological parameters and the light-shielding efficiency of the layers. Especially scattering domains in TSFD were not investigated yet. Thus, the overall objective of the present investigation is to determine additive, and thus scattering domain size and distribution in TSFD. Specific focus is given to the effect of additive type on the formation of scattering domains. A morphological characterization of the thermotropic layers is performed applying Atomic Force Microscopy (AFM) in phase imaging mode. Furthermore relationships between the scattering domain size and the light-shielding properties of the thermotropic layers are established.

2. Materials and Sample Preparation

For the present investigation a UV curing resin (resin A) and 4 non-polar thermotropic additives exhibiting switching temperatures between 45 and 85°C were selected (additives 2 to 5). According to previous publications (Resch et al., 2008a; Resch et al., 2008c) the denotation of the additive types starts with 2. The molecular weight of the additives increases successively from additive type 2 to 5 (Resch et al., 2008c). Thermotropic layers were produced by dissolving a thermotropic additive in a photo-cross-linkable resin material composed of 57 wt.% oligomer, 40 wt.% reactive diluent, and 3 wt.% photoinitiator. The additive concentration was 5 wt%. The dissolution of the thermotropic additive in the resins was filled into an intervening space located between two glass panes, which were sealed around the edge. Afterwards the mixture was cured by UV-radiation (Ultra

Vitalux, Osram GmbH, Muenchen, GER) for 5 minutes. Film thickness was 800 µm. As to the nomenclature A-2 indicates a film based on resin A containing additive type 2, for example.

3. Morphological Characterization

For the investigations concerning layer morphology, cross-sections of the samples were prepared using an ultramicrotome (Leica, GER). A comprehensive characterization as to scattering domain sizes and shapes was done applying Atomic Force Mircroscopy (AFM). Specific focus was given to the generation of high resolution phase images. Due to the fact that an AFM phase image represents the phase lag between the agitating oscillation and the detected cantilever oscillation, the differentiation between hard (i.e., resin) and soft (i.e., additive) sample areas is possible. AFM was performed in tapping mode (frequency: ~80 kHz) with a MFP 3D (Asylum Research, Santa Barbara, CA, USA). Phase images with a lateral resolution below 0.1 µm were recorded under ambient conditions with the “fast” scan axis parallel to the machine direction of the film. Sharpened Si NCH tips with a tip radius <10 nm and an opening angle of 18° were used.

4. Results and Discussion

In the AFM height images presented in Figs. 1 to 4 brighter colors indicate feature heights. In the corresponding phase images, dark colors represent a smaller phase lag and bright colors a larger phase shift. According to this, the darker areas represent the softer additive particles, and thus scattering domains, and the resin matrix appears bright.

In Fig. 1 representative 50x50 µm² AFM height and phase images of thermotropic layer A-2 are depicted. The characteristic features of the height images (Fig. 1a) are roughly spherical particles which are distributed randomly across the film thickness. In the phase image (Fig. 1b) these structures show a smaller phase contrast compared to the surrounding material and are thus softer. Applying Raman microscopy it was ascertained that these features can be attributed to the additive and represent scattering domains. The uniform distribution of the scattering domains is in good agreement with additive concentrations on the film surface determined by Attenuated Total Reflectance Spectroscopy in Resch et al. (2008a). The scattering particle size ranges from 0.4 to 3 µm.

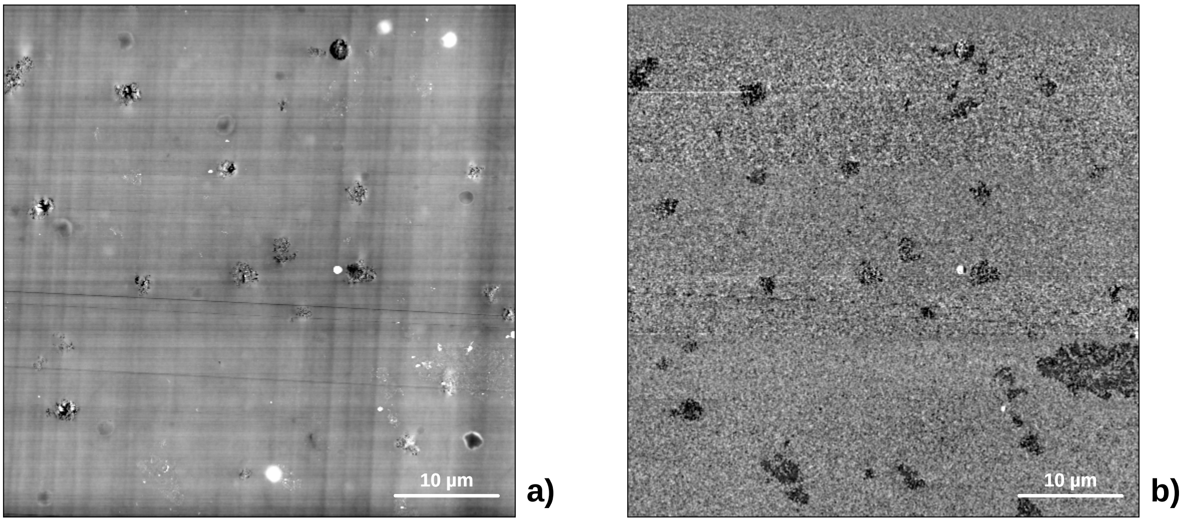


Fig. 1: **a)** 50x50 µm² AFM height image of thermotropic layer A-2 and **b)** corresponding phase image.

Figure 2 shows high resolution AFM height and phase images (5x5 µm²) of a scattering domain of thermotropic layer A-2. The domain consists of numerous smaller additive particles (primary particles), with sizes between 50 and 200 nm. The aggregation of the wax primary particles results in the formation of microscopic scattering domains with dimensions up to 3 µm.

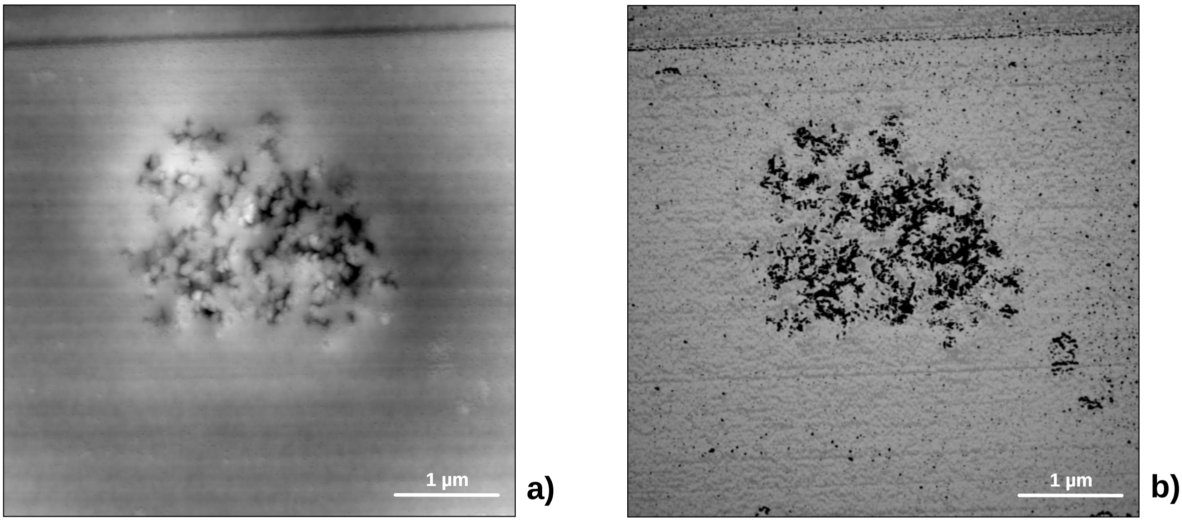


Fig. 2: **a)** High resolution AFM height image of thermotropic layer A-2 and **b)** corresponding phase image.

For high back scattering efficiency in the opaque state spherical domains with diameters between 200 and 400 nm are optimal (Nitz, 1999; Nitz and Wilson, 2008). Larger particles lead to increased diffuse forward scattering. The reduction in solar transmittance detected by UV/Vis/NIR spectroscopy of layer A-2 is 6% (Resch, 2008a; Resch 2008c). The diffuse transmittance increases by 24% above the switching threshold (Resch, 2008a; Resch, 2008b). The moderate reduction of the hemispheric transmittance along with the significant increase of the diffuse transmittance can be attributed to the inappropriate scattering domain sizes.

In Fig. 3 an AFM height and phase image of thermotropic layer A-3 is presented. These images are representative for thermotropic materials A-3, A-4 and A-5. The spherical structures observable in the height image can be attributed to the carrier film used for collecting the thin sample slices after preparation on the ultramicrotome. In the height image (Fig. 3a) also anisotropic features are observable. These structures consist of a lower center seamed by an elevated region on both sides and are distributed uniformly across the film thickness. Most likely the recorded features are an indication for contorted disk-like domains within the layer. In the corresponding phase image (Fig. 3b) a smaller phase lag is detectable for the disk-like structures.

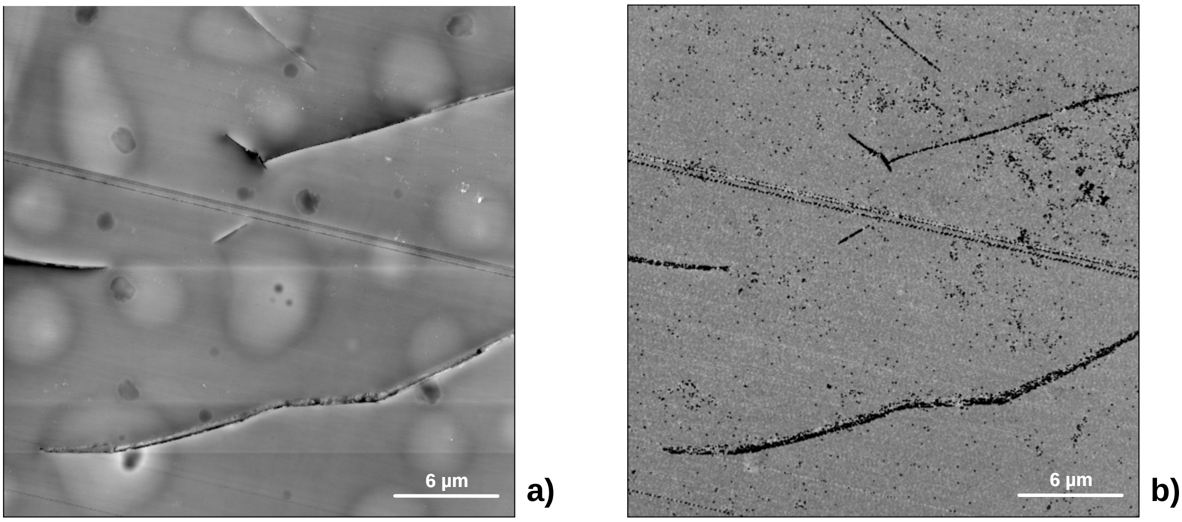


Fig. 3: **a)** 30x30 µm² AFM height image of thermotropic layer A-3 and **b)** corresponding phase image.

Applying also Transmission Electron Microscopy and Raman microscopy it was confirmed that these features represent the waxy scattering domains. The additive's molecular weight increases continuously from material type 2 to 5. Compared to the short-chain additive 2, waxes with longer aliphatic chains (additives 3 to 5) tend towards the formation of scattering particles resembling contorted disks in the considered matrix material.

Figure 4 illustrates AFM height and phase images of disk-like domains of thermotropic layers A-3, A-4 and A-5 in higher magnification. Various shapes of the domains are apparent. The additives develop branched (Fig. 4a and b), as well as curved (Fig. 4c and d) or straight (Fig. 4e and f) scattering features. In the height image of sample A-3 (Fig. 4a) a groove-like structure of the scattering domain is evident. In the center of the feature a distinct disruption (dark colors) is detectable. However, what now appears to be a groove may initially be generated by and filled with the additive. Presumably during sample preparation additive is released. A variable thickness of the disk-like feature ranging from 100 to 200 nm is observable. The phase image does not show any phase lag to the surrounding matrix material in the center of the feature (Fig. 4b). The additive is concentrated in the fringe, indicated by the smaller phase shift.

The AFM height images of thermotropic layer A-4 given in Fig. 4c a reveals an even more pronounced groove-like appearance of the scattering domain. Furthermore the elevated region seaming the feature is developed stronger compared to the feature given in Fig. 4a. The domain thickness is narrowing from 400 nm to 300 nm. In the corresponding phase image (Fig. 4d) hardly any additive areas are discernible, especially in the disrupted center of the feature. The highest additive concentrations occur in regions which appear elevated in the height image.

However, additive does not necessarily release by sample preparation, as observable in Fig. 4e that depicts a high resolution AFM height image of a scattering domain in thermotropic layer A-5. The scattering feature displays a slight elevation (~200 nm in height). This elevated region exhibits a stronger phase contrast compared to the adjacent plane area in the left of the domain. This is an indication for higher additive concentration in the elevated region. The overall thickness of the feature given in Figs. 4e and f is 300 nm. In general no differences in scattering domain size are detectable for the layers A-3, A-4 and A-5. The diameter of the contorted disks is below 50 µm. The thickness ranges between 100 and 400 nm.

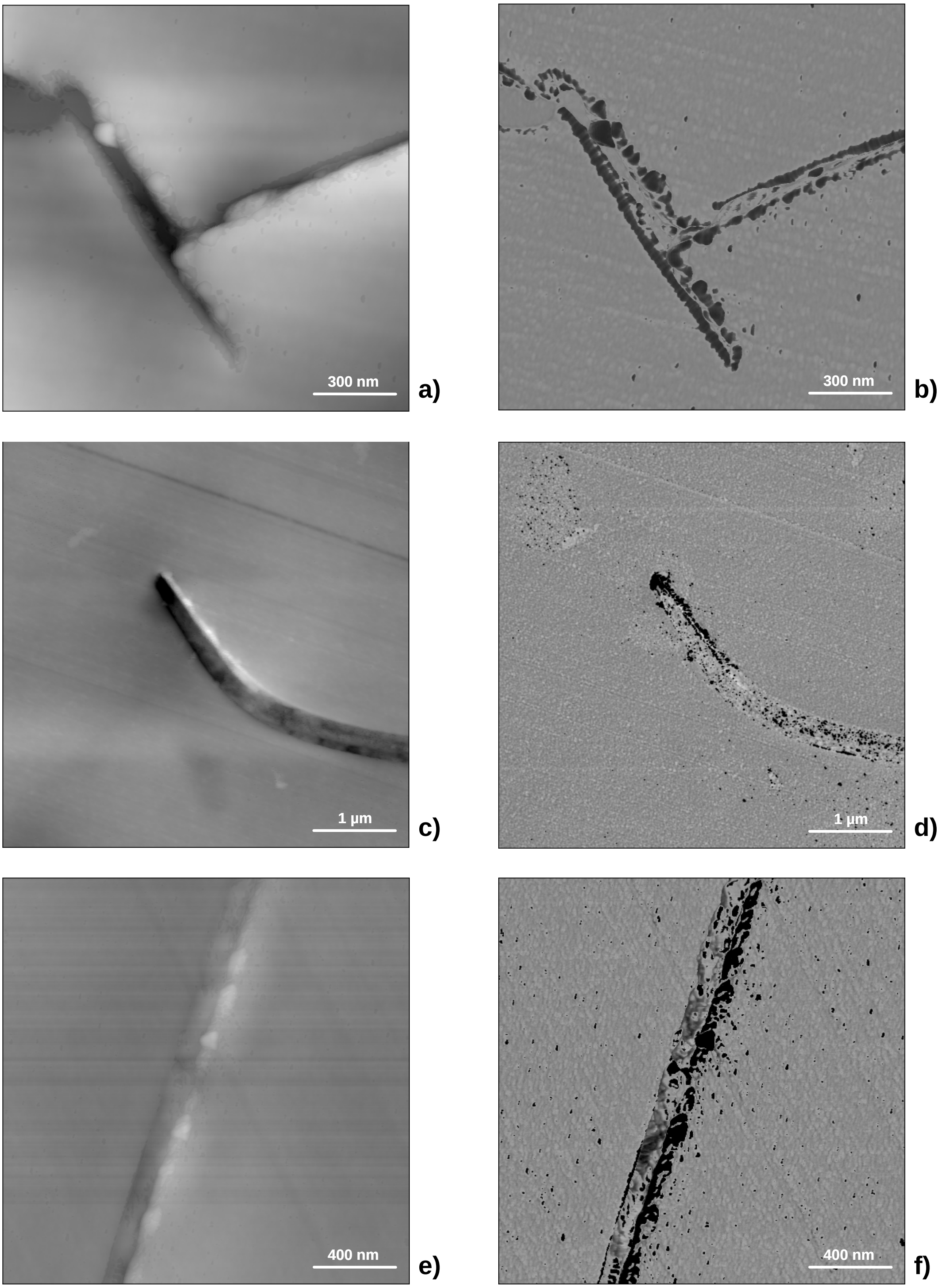


Fig. 4: High resolution AFM images of disk-like scattering domains; **a)** height image of thermotropic layer A-3 and **b)** corresponding phase image, **c)** height image of thermotropic layer A-4 and **d)** corresponding phase image, **e)** height image of thermotropic layer A-5 and **f)** corresponding phase image.

A tendency is observable that thermotropic layers exhibiting disk-like scattering domains show better light-shielding properties than thermofunctional materials displaying roughly spherical particles. For thermotropic layers A-3, A-4 and A-5 a reduction of the hemispheric solar transmittance by 9 to 10% is reported (Resch et al., 2008c). The diffuse solar transmittance increases by 15 to 23% above the switching threshold. The measured thickness of the contorted disks is in agreement with an ideal domain size for back-scattering (Nitz, 1999; Nitz and Wilson, 2008). Hence, incoming radiation is scattered more effectively for TSFD layers A-3, A-4 and A-5 than for layer A-2.

5. Summary and Conclusion

Within this paper scattering domains in thermotropic systems with fixed domains (TSFD) were investigated applying Atomic Force Microscopy phase imaging. Thermotropic layers being formulated with additives exhibiting a short chain length displayed roughly spherical scattering particles with dimensions between 0.5 and 3 µm. For functional material types containing additives with high molecular weight, anisotropic scattering domains resembling contorted disks showing a diameter up to 50 µm and a thickness between 100 and 400 nm were ascertained. A uniform distribution of the scattering domains across the film thickness was detected. The changes in hemispheric and diffuse solar transmittance of the thermotropic layers above the switching threshold were found to be in good agreement with the particle size and shape. Layers exhibiting large spherical scattering domains displayed a moderate reduction in the hemispheric solar transmittance by 6% along with a significant increase of the diffuse solar transmittance by 24%. Thermofunctional layers showing disk-like scattering features possessed better light-shielding properties (hemispheric transmittance -9 to 10%; diffuse transmittance +15 to 23%). However, for solar collector applications a reduction in hemispheric transmittance by at least 25% is required. Hence, further research should focus on an adjustment of the scattering domain size, shape, and distribution for optimizing the light-shielding properties.

Acknowledgements

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH within the framework of the Non K_{plus} Program.

This work is funded by the State Government of Styria, Department *Zukunftsfonds Steiermark*. ZUKUNFTSfonds STEIERMARK Das Land Steiermark

The authors wish to express their acknowledgements to Cytec Surface Specialties (Drogenbos, BEL), Sasol Germany GmbH (Hamburg, GER) and Chemson Polymer Additive AG (Arnoldstein, AUT), for providing the materials.

Special thanks go to the Austrian Center for Electron Microscopy and Nanoanalysis (Graz, AUT) for sample preparation.

References

Nitz, P., Hartwig, H., 2005. Solar control with thermotropic layers, Solar Energy 79 573-582.

Nitz, P. (1999). Optische Modellierung und Vermessung thermotroper Systeme, PhD Thesis, Fakultät fuer Physik, Albert-Ludwigs-Universität Freiburg im Breisgau, DE.

Nitz, P., Wilson, H.R., 2008. Modellierung thermotroper Materialien, in Proc. 2nd Leobner Symposium Polymeric Solar Materials, 7 - 8 February, Leoben, AT, pp. XIII – 1-6 .

Resch, K., Wallner, G.M., 2007. Thermotropic resin systems: Relationships between formulation parameters, material structure and optical properties, in: Proc. Solar World Congress 2007, 18 - 21 September 2007, Beijing, CN, pp. 541-545.

Resch, K., Hausner, R., Wallner, G.M., 2007. All Polymeric flat-plate Collector – Potential of Thermotropic Layers to Prevent Overheating, in Proc. Solar World Congress 2007, 18 - 21 September 2007, Beijing, CN, pp. 56-565.

Resch, K., Wallner, G.M., Lang, R.W., 2008a. Spectroscopic investigations of phase- separated thermotropic layers based on UV cured acrylate resins, Macromolecular Symposia 265, 49-60.

Resch, K., Wallner, G.M., 2008b. Thermotropic layers for flat-plate collectors – a review of various concepts for overheating protection with polymeric materials. In press for Solar Energy Materials and Solar Cells.

Resch, K., Wallner, G.M., Hausner, R., 2008c. Phase separated thermotropic layers based on UV cured acrylate resins – structure-property relationships, submitted to Solar Energy.

Seeboth, A., Schneider, J., Patzak, A., 2000. Materials for intelligent sun protecting glazing, Solar Energy Materials and Solar Cells 60, 263 - 277.

Wallner, G.M., Resch, K., Hausner, R., 2008. Property and performance requirements for thermotropic layers to prevent overheating in an all polymeric flat-plate collector, Solar Energy Materials and Solar Cells 92, 614-620.

5 Structure-Property Correlations of Thermotropic Polymer Systems with Fixed Domains for Solar Collector Applications

5.1 Introduction

To date 5 patents were published which describe the preparation of thermotropic systems with fixed domains (TSFD) based on a thermoset resin matrix (Dabisch, 1978; Meinhardt et al., 1996; Bicer et al., 1997; Bicer et al., 2000; Schwitalla et al., 2002). Interestingly, only a single scientific publication briefly discussing this subject seems to exist (Wilson, 2000). A fundamental understanding of the physical relationships between the properties of the basic material types used for layer production and the performance characteristics of the thermotropic systems was not yet established. Thus, material development so far was not done considering polymer physics and applying a systematic polymer science approach. Efficient and systematic development and optimization of TSFD, however, requires basic knowledge on interrelationships between properties of formulation ingredients and the switching characteristics of the thermotropic layers.

Hence, the overall objective of this chapter is to generate information on formulation parameters affecting the light-shielding properties of TSFD, which shall provide the basis for further material development. This includes the establishment of structure-property correlations, with specific focus on

- relationships between the switching temperature of the additive and the thermotropic layer,
- relationships between transition temperature range of the thermotropic layers and the thermal transitions of the additive,
- the effect of the additive type and molecular mass on the light-shielding efficiency of the thermotropic layer, and
- the effect of resin type and its interactions with additive on the light-shielding efficiency of the thermotropic layer.

Various TSFD are prepared by variation of base resin and additive type and concentration. In total three different UV-curable matrix materials and six polar and non-polar additive types are selected. The matrix oligomers include a polyester acrylate (Material A), a urethane acrylate (Material B) and an epoxy acrylate (Material C). The matrix materials were provided by Cytec Surface Specialties (Drogenbos, BE). As additive types paraffin waxes with different melting temperatures (Additives 2 to 5) and an ester of an alcohol (Additive 6) are considered. The additives were provided by Sasol Germany GmbH (Hamburg, DE) and Chemson Polymer Additive AG (Arnoldstein, AT), respectively. Functional films with additive concentrations of 5 and 7 m% are investigated.

Apart from the determination of polymer-physical factors affecting the properties of TSFD, investigations concerning the overheating protection performance of the thermotropic layers in the solar collector are essential for optimizing material properties. In an experimental study by Wendker (1999) thermotropic polymer blends prototype-layers were applied for overheating protection purposes in a solar collector with metal absorber and transparent insulating glazing. The materials controlled maximum absorber temperatures to values below 115°C but exhibited insufficient long-term stability and inappropriate switching temperatures. The overheating protection efficiency of TSFD prototype-layers in solar collectors was not investigated yet.

Thus within this chapter furthermore the overheating protection capability of TSFD prototype-layers for an all-polymeric flat-plate collector with twin-wall sheet glazing and black absorber is evaluated applying theoretical modeling. Focus is directed towards

- the effect of TSFD on collector stagnation temperature, and
- the effect of TSFD on overall collector efficiency.

The theoretical modeling is performed using a software generated by AEE – Institute for Sustainable Developments (AEE-INTEC; Gleisdorf, AUT). The experiments are carried out by Dipl.-Ing. Robert Hausner (AEE–INTEC). The software provides a comprehensive theoretical mathematical description of flat-plate solar collector performance and allows for the evaluation of collector conversion factors and for the determination of efficiency graphs. Details concerning the modeling software and the chosen collector configuration are given in a publication closely related to this thesis (Wallner et al., 2008).

5.2 Paper 5

Paper 5: Phase separated thermotropic layers based on UV cured acrylate resins – Structure-property relationships
by K. Resch, G.M. Wallner and R. Hausner
(submitted to: *Solar Energy*)

This paper includes a comprehensive investigation concerning the effect of resin and additive type and their interactions on the light-shielding performance of numerous TSFD. Structure-property relationships are established, which provide a basis for further material development and optimization. Switching temperature, switching process and hemispheric and diffuse solar transmittances in the clear and opaque state of TSFD are determined applying UV/Vis/NIR spectroscopy. The switching temperature and switching process of the layers are compared to thermal transitions of the additive deduced from Differential Scanning Calorimetry (DSC). Furthermore, the capability of selected TSFD to reduce stagnation temperatures in an all-polymeric flat-plate collector is described applying theoretical modeling.

5.2 Key Literature

Bicer, T., Goedeke, H., Werner, J., Schoenfeld, U. (1997). EP 0946443.

Bicer, T., Schwitalla, C., Goedeke, H. (2000). EP 1095080.

Dabisch, W. (1978). EP 0000868.

Meinhardt, S., Schoenfeld, U, Goedeke, H. (1996). DE 4433090.

Schwitalla, C., Goedeke, H., Koenig, H. (2002). EP 1258504.

Wallner, G.M., Resch, K., Hausner, R. (2008). Solar Energy Materials and Solar Cells **92**, 614.

Wendker, K. (1998). „Untersuchungen zum Einsatz thermotroper Schichten in Sonnenkollektoren“, Diploma Thesis, Fraunhofer Institute for Solar Energy Systems, Freiburg, DE.

Wilson, H.R. (2000). Functional Materials – EUROMAT 99 **13**, 221.

Phase separated thermotropic layers based on UV cured acrylate resins – Structure-property relationships

Katharina Resch[1], Gernot M. Wallner[2], Robert Hausner[3]

[1] Polymer Competence Center Leoben GmbH
Roseggerstrasse 12, 8700 Leoben, Austria

[2] Institute of Materials Science and Testing of Plastics, University of Leoben
Franz-Josef Strasse 18, 8700 Leoben, Austria

[3] AEE – Institut fuer Nachhaltige Technologien (AEE-INTEC)
Feldgasse 19, 8200 Gleisdorf, Austria

Abstract

This paper focuses on the effect of material composition on the overheating protection properties of thermotropic systems with fixed domains for solar thermal collectors. Numerous functional layers were prepared by a variation of base resin and of thermotropic additives. A detailed investigation of optical properties, switching temperature and switching process was performed applying UV/Vis/NIR spectroscopy. Thermal transitions of both the thermotropic layers and the additives used were determined by Differential Scanning Calorimetry (DSC). The capability to reduce stagnation temperatures in an all-polymeric flat-plate collector was evaluated by theoretical modeling. The produced thermotropic layers showed a hemispheric transmittance between 76 and 87% in clear state. Above the switching threshold the transmittance changed by 1 to 18% to values between 62 and 85%. The layers exhibited switching temperatures between 40 and 80°C and transition temperature ranges between 10 and 25 K. A particular effect of the resins glass transition temperature on the reduction of the hemispheric solar transmittance above the switching threshold was ascertained. The hemispheric switching range was found to increase with increasing molecular weight of the non-polar additive types. The comparison of the switching performance with the additives thermal transitions revealed a good correlation. Theoretical modeling showed that by using selected thermotropic layers the maximum absorber temperatures can be limited to temperatures below 130°C.

Keywords: overheating protection, thermotropic resin, UV/Vis/NIR spectroscopy, switching performance, modeling

1. Introduction

The application of polymeric materials in active solar thermal systems is gaining increasing in importance and interest. Polymeric components in solar collectors offer new possibilities concerning system innovations and collector design and may lead to a significant reduction of overall system costs. However, as shown by theoretical modeling stagnation temperatures up to 160°C can occur in an all-polymeric flat-plate collector with twin-wall sheet glazing and black absorber (Resch et al., 2007; Wallner et al., 2008). Thus a key challenge in the application of plastics in solar thermal systems is to maintain system durability for extended lifetimes. Especially if cost-efficient plastics with maximum operating temperatures of 130°C are applied as absorber materials an adequate overheating protection is required. A feasible way to reduce maximum absorber temperatures is the use of thermotropic materials either in the glazing or on the absorber (Khan and Brunger, 1997; Resch et al., 2007; Wallner et al., 2008). Thermotropic layers change their light transmission behavior from highly transparent to light diffusing upon reaching a certain threshold temperature (e.g. Seeboth et al., 2000; Nitz and Hartwig, 2005; Resch and Wallner 2008). For thermotropic glazings and thermotropic absorbers switching temperatures between 55 and 60°C and 75 and 80°C are required, respectively (Wallner et al., 2008). To ensure sufficient collector efficiency the solar transmittance should exceed 85% in the clear state. Adequate overheating protection is obtained with layers that exhibit a residual solar transmittance below 60% in the opaque state (Resch et al., 2007; Wallner et al., 2008).

Thermotropic systems with fixed domains (TSFD) that consist of a thermotropic additive dispersed in a resin matrix are currently evaluated for the application in solar thermal collectors (Resch and Wallner, 2007; Resch et al., 2008). Spectroscopic investigations as to optical and morphological properties revealed inappropriate switching temperatures and a moderate reduction in hemispheric solar transmittance (Resch et al., 2008). Thus for overheating protection of solar collectors the transition temperature and the light-shielding performance of the functional materials have to be improved. The switching temperature is dependent on the thermal transition of the additives. Back scattering efficiency is affected by the differences in refractive index between resin and additive as well as by scattering domain size and distribution (Nitz, 1999; Resch et al., 2008). However, the development of scattering domains may be strongly determined by the resin type used and its interactions with the additive. Hence, the main objective of the present investigation is to describe the impact of resin and additive type and their interactions on the light-shielding efficiency of TSFD performing a comprehensive polymer-physical characterization. Specific focus is directed towards the establishment of structure-property relationships which shall provide a basis for a systematic optimization of TSFD. Numerous TSFD domains are prepared using three different base resins and five thermotropic additives. The thermotropic layers are characterized as to switching performance applying UV/Vis/NIR spectroscopy. The switching performance is compared to thermal transitions of the thermotropic additive. Relationships between the resin and additive type and the light-shielding properties of thermotropic layers are established. Furthermore the effect of selected TSFD on the collector efficiency is evaluated applying theoretical modeling.

2. Materials

Various thermotropic layers were produced by dissolving a thermotropic additive in a photo-cross-linkable resin material composed of 57 m% oligomer, 40 m% reactive diluent, and 3 m% photoinitiator. This dissolution was filled into an intervening space located between two glass panes, which were sealed around the edge. After irradiation with UV light (Ultra Vitalux, Osram GmbH, Muenchen, GER) for 5 minutes and removal of the glass panes, freestanding layers with a thickness of 800 µm were obtained. For the present investigation 3 different acrylate oligomers serving as the main component of the matrix material (resin types A, B and C) were selected. The resins differ in chemical basis and cross-linking density. Whereas resin type B exhibits a wide meshed network and a glass transition temperature of ~25°C, resin types A and C feature a higher cross-linking density and glass transition temperatures of ~55 and ~60°C, respectively. As thermotropic component 5 different thermotropic additives with switching temperatures between 45 and 90°C were used (additive types 2, 3, 4, 5: non-polar; additive type 6: polar). To be in accordance with a previous published paper (Resch et al., 2008) the denotation of the additive types starts with 2. Theoretical additive concentrations of 5 m% and 7 m% were chosen for the preparation of the films. As to the nomenclature, for example A-2-5 indicates the thermotropic layer based on resin type A and being formulated with additive type 2 in a concentration of 5 m%.

3. Material Characterization

3.1 Experimental

3.1.1 Differential Scanning Calorimetry (DSC)

The switching temperatures of the additives and the produced thermotropic layers with additive concentrations of 5 m% were determined by Differential Scanning Calorimetry (DSC). Thermograms were recorded under static air on a Mettler Toledo DSC823e (Schwarzenbach, CH) in a temperature range between 0°C and 130°C applying a heating rate of 10 K/min. The sample mass was 10 ± 1 mg. The melting temperature was evaluated according to ISO 11357-3. The data were averaged over three measurements.

3.1.2 UV/Vis/NIR Spectroscopy

Solar transmittance in clear and opaque state, switching temperature and switching process of the thermotropic layers were determined applying UV/Vis/NIR spectroscopy. A double beam UV/Vis/NIR spectrophotometer (Lambda 950, Perkin Elmer Instruments GmbH, Ueberlingen, GER) equipped with an Ulbricht-sphere (diameter 150 mm) was adapted by a heating stage to adjust the sample temperature. For the given measurement apparatus the radiation passing through the specimen outside a cone of approximately 5° relative to the incident beam direction is defined as diffuse (scattered) component. Hemispheric and diffuse transmittance were recorded at normal incidence in the spectral region between 250 and 2500 nm in steps of 5 K from 25°C to 100°C. Prior to the measurements the sample was maintained at the selected temperature for 10 minutes. The integral solar transmittance was determined by weighting the recorded spectral data in steps of 5 nm by the AM 1.5 global solar irradiance source function, given in Bird and Hulstrom (1983). The obtained data were corrected for radiative losses due to the measurement setup according to Resch et al. (2008).

3.2 Results and Discussion

The switching process in the thermotropic layer is induced by the melting of the additive. However, the melting point of the bulk additive does not necessarily correlate with the melting temperature of the additive dispersed in the matrix material (Dabisch, 1978). Thus in Fig. 1 melting temperatures of the additives in bulk form and dispersed in the thermotropic materials in a concentration of 5 m% are compared. For the pure additives melting peak temperatures between 54 and 86°C were determined. For the non-polar additive types 2 to 5 a continuous increase of the melting temperature from material type 2 to material type 5 is observable. This is an indication for increasing molecular weight. The high melting temperature of additive type 6 can be ascribed not necessarily to the molecular weight. In this polar additive strong intramolecular interactions are active. Except for the thermotropic layer A-3-5 the melting peak temperature of the additive dispersed within the resin is between 2 and 5°C lower than in its bulk form. These differences in melting point are most likely related to additive size. The particle size of the additive within the thermotropic layer is significantly smaller (<3 µm) than in its bulk form (50-700 µm). The resulting larger surface to volume ratio and thus lower cohesive energy leads to a decrease of the materials melting point (Sakai, 1996; Riegler and Koehler, 2007). For the polar additive type 6 the smallest shifts in melting temperatures are discernible. For this material type stronger intermolecular interactions occur due to chemical similarities between resin and additive, which cause the melting temperature to increase slightly. The smallest deviations in melting temperature are observable for additives dispersed in resin type B. The wide-meshed network of resin type B may benefit additive mobility and thus the development of larger scattering domains. For the non-polar additive types 2 to 5 the deviations increase with increasing melting temperature and thus molecular weight. The melting peak temperature of additive type 3 is 17°C higher than in its bulk form if dispersed in resin type A. Additive type 3 melts in the temperature range between 40 and 80°C with a distinct maximum at 60°C. However, in thermotropic layer A-3-5 molecule chains contributing to the melting region between 70 and 80°C are predominantly active. This leads to a shift of the switching temperature.

To limit collector stagnation temperatures to ~80°C thermotropic glazings with switching temperatures between 55 and 60°C are required. For thermotropic absorbers the switching temperature should range between 75 and 80°C (Resch et al., 2007; Wallner et al., 2008). According to the transition temperatures deducible from Fig. 1 thermotropic layers produced with additive types 2 and 3 are suited for the application in the collector glazing (except layer A-3-5, which is more suited for the thermotropic absorber). Thermotropic layers formulated with additive types 4 to 6 are more appropriate for the use on the absorber.

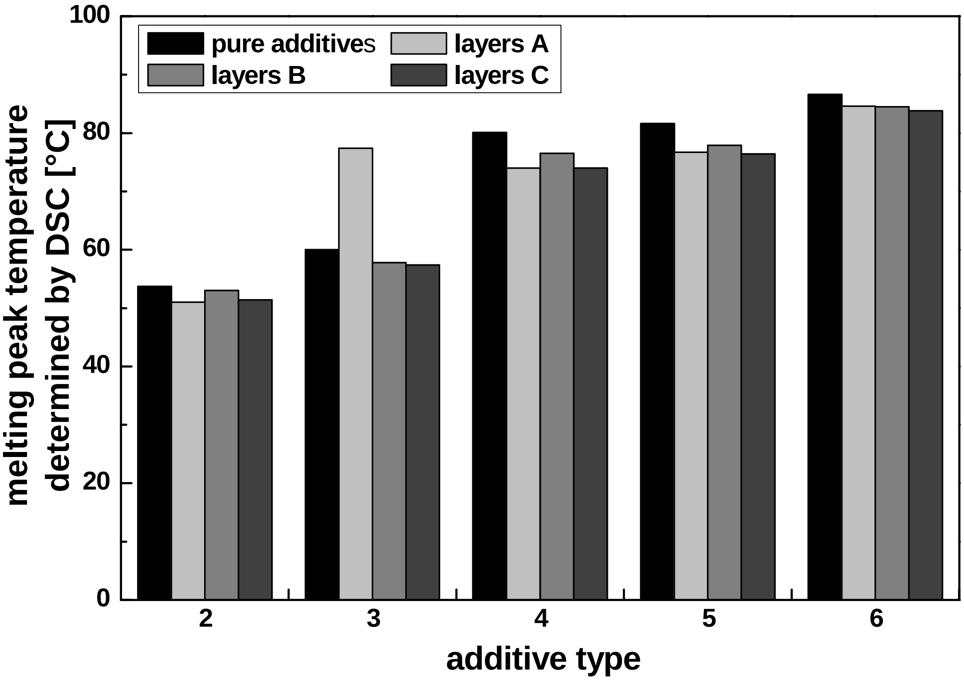


Fig. 1: Melting peak temperatures of additives in pure form and dispersed in the resins in a concentration of 5 m%.

Figure 2 illustrates the integral hemispheric solar transmittance along with the diffuse fraction for the investigated thermotropic layers in clear and opaque state. Below the switching temperature the samples exhibit a hemispheric solar transmittance between 76% and 87%. For the diffuse transmittance considerable differences between the various material formulations are discernible. The values range from 14 to 71%. Films with a diffuse transmittance exceeding 40% (A-2-5, A-4-5, C-6-5, C-6-7) exhibit a hazy appearance already in the clear state. The lowest diffuse transmittance in the clear state is observable for thermotropic layers based on resin type B. Compared to thermotropic layers based on resin type A, functional materials with resin C basis tend to show lower diffuse transmittance if formulated with the non-polar additive types 2 to 5. This is in reverse for layers containing additive type 6. For film types being formulated with additive types 2 and 3 an increase of the additive content from 5 to 7 m% leads to a slight decrease of the overall transmittance. For thermotropic layers produced with additive types 4 and 5 the additive concentration does not affect the hemispheric transmittance (except layers B-5). The minor impact of the additive concentration on the hemispheric transmittance in the clear state is attributable to a limited dissolving power of the resins for the additives. This effect is even more pronounced if the molecular weight of the additives increases, especially for non-polar additives. Nevertheless, a tendency is observable that an increase of the additive concentration from 5 to 7 m% is associated by an increase of the diffuse transmittance.

The overheating protection properties of the thermotropic layers are determined by the reduction of hemispheric transmittance in the scattering state. Above the switching temperature the hemispheric transmittance changes by 1 to 18% to values ranging between 62 and 85%. The data presented in Fig. 2 show, that no significant effect of the additive concentration on the hemispheric switching range is discernible if 5 and 7 m% are considered. Previous examinations revealed a considerable increase of the light-shielding efficiency by increasing the additive concentration from 2 to 5 m%. This indicates that the maximum additive content for the considered thermotropic layers is about 5 m%. For layers based on resin B and being formulated with additive types 4 to 6 even a slight increase of the hemispheric transmittance above the switching threshold is detectable. Whereas thermotropic layers based on resin type C tend to exhibit the most significant decrease of the hemispheric transmittance, for layers produced from resin type B the lowest changes are discernible. Compared to resin type B resin types A and C exhibit higher cross-linking densities and decreased chain mobility (higher glass transition temperature). Probably these properties facilitate the precipitation of the additive in dimensions required for back-scattering. A tendency is observable that for thermotropic layers based on resin types A and C the light-shielding efficiency increases with increasing molecular weight of the non-polar additive types 2 to 5. This can most likely be attributed to a limited mobility of high molecular weight additives in the dense network, which results in the formation of scattering domain sizes required for maximizing solar back-scattering efficiency. Hence, if additive types with lower molecular weight and thus lower switching temperature are used, to enhance light-shielding efficiency resin types with still higher cross-linking densities and glass transition temperature have to be used. With increasing molecular weight of the non-polar additives also the deviations in melting peak temperature of the additives in bulk form and dispersed in the resin were detected to increase (see Fig. 1). However, no distinct correlation between the differences in the melting peak temperature and the thermotropic layers light-shielding efficiency can be established. Thermotropic layers based on resin type C and additive type 6 exhibit the most significant reduction of the hemispheric transmittance above the switching threshold. Independent on the additive concentration the transmittance changes by 14%. In contrast to the other layers considered within the present investigation for these thermotropic films the reduction of the hemispheric transmittance is associated by a decrease of the diffuse transmittance. This indicates that the scattering domain size in these layers is ideal for back scattering (diameters between 200 and 400 nm required). Generally, scattering particles with diameters exceeding 400 nm lead to an increase of diffuse forward scattering above the switching threshold. This is the case for the other layers, which show a significant increase of the diffuse transmittance by 9 to 61% to values between 36 and 78% above the switching temperature. Thermotropic layers produced from resin C show more significant changes of diffuse transmittance than functional materials with resin A basis. The most distinct changes are observable for thermotropic layers based on resin type B. Thus a wide-meshed network and low glass transition temperature (characteristic for resin type B) leads to the development of larger scattering domains, which benefit forward scattering.

For the application of cost-efficient plastics as absorber materials in an all-polymeric solar collector a hemispheric transmittance of minimum 85% in clear state and maximum 60% in opaque state is required. As to the hemispheric switching range thermotropic materials based on resin type C and being formulated with additive type 6 are the most promising layers for overheating protection of a solar collector (14% and 18%). However, the solar transmittance in clear state needs to be improved (actual 78% and 83%). Furthermore functional materials based on resin type A and being formulated with additive types 3 to 5 and produced from resin type C with additive types 4 and 5 may be appropriate to reduce stagnation temperatures. For these materials especially the switching range has to be increased.

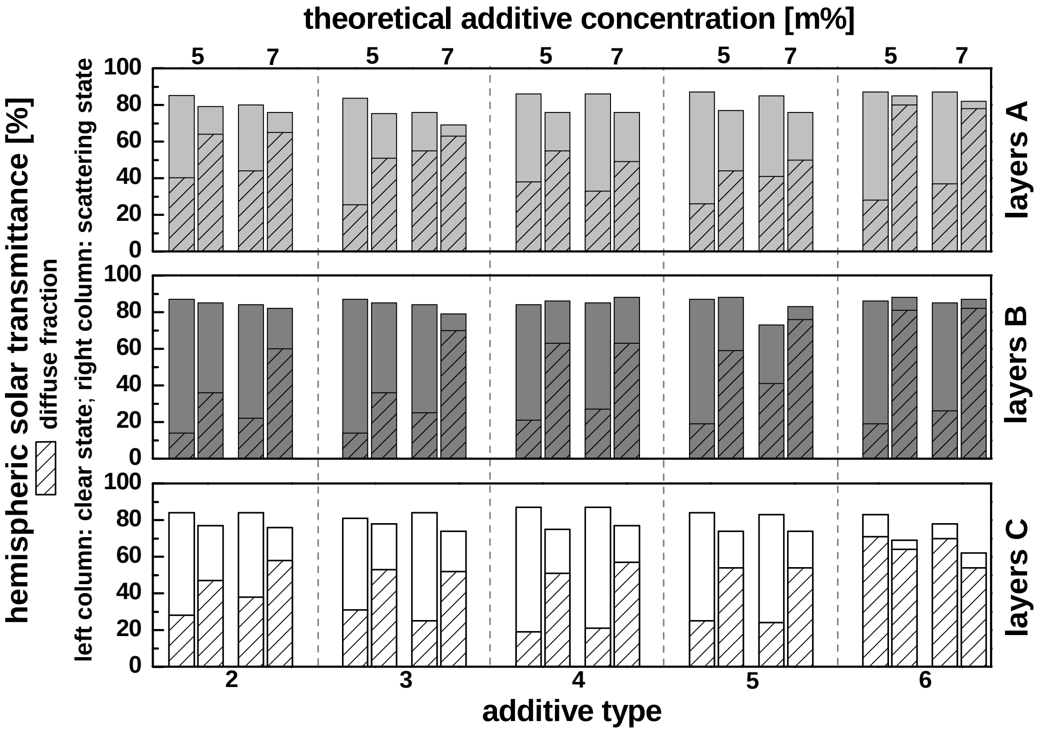


Fig. 2: Hemispheric solar transmittance and diffuse fraction of thermotropic layers in clear (left column) and opaque state (right column) for different additive concentrations; top: layers based on resin A; mid: layers based on resin B; bottom: layers based on resin C.

For the investigated layers the temperature induced change in diffuse transmittance is more distinct than the change in the hemispheric transmittance. Thus to describe the switching process of the thermotropic layers in Figs. 4 to 7 the diffuse solar transmittance is plotted as a function of temperature (additive concentration 5 m%). The various layers show switching temperatures between 45 and 80°C. For thermotropic layers A-2, B-2, C-2, A-3 and B-5 the diffuse solar transmittance changes within a small temperature range below 15 K. A reasonable switching progress with transition ranges of 15 to 20 K is observable for functional layers A-4, A-5, C-5 and C-6. Thermotropic layers B-3, C-3, B-4, C-4, A-6 and B-6 exhibit a broad transition range exceeding 20 K. In general for thermotropic layers that shall be applied to prevent overheating of a solar collector a steep switching process within a small temperature range is required. Thermotropic layers with a broad transition range of 20 K are less suited for solar collector applications.

In Figs. 3 to 7 the switching characteristics of the thermotropic layers are compared to the thermal transition of the additives (in bulk form). For all films it is observable that at the onset of the additive's melting peak the diffuse transmittance increases significantly. Subsequently the switching proceeds with the melting of the additive. The thermotropic layer reaches its final scattering state once the additive is in a fully melted state. For additive type 2 (Fig. 3) besides the melting peak between 40 and 50°C an endothermic effect at lower temperatures (25-35°C) is observable. This peak can be attributed to a phase transition in the crystalline structure from orthorhombic to hexagonal (Hammami und Mehrotra, 1995; Meyer et al., 2005). Regarding the switching characteristics of the thermotropic layers being formulated with additive type 2 the change in crystalline order leads to a slight increase of the diffuse solar transmittance.

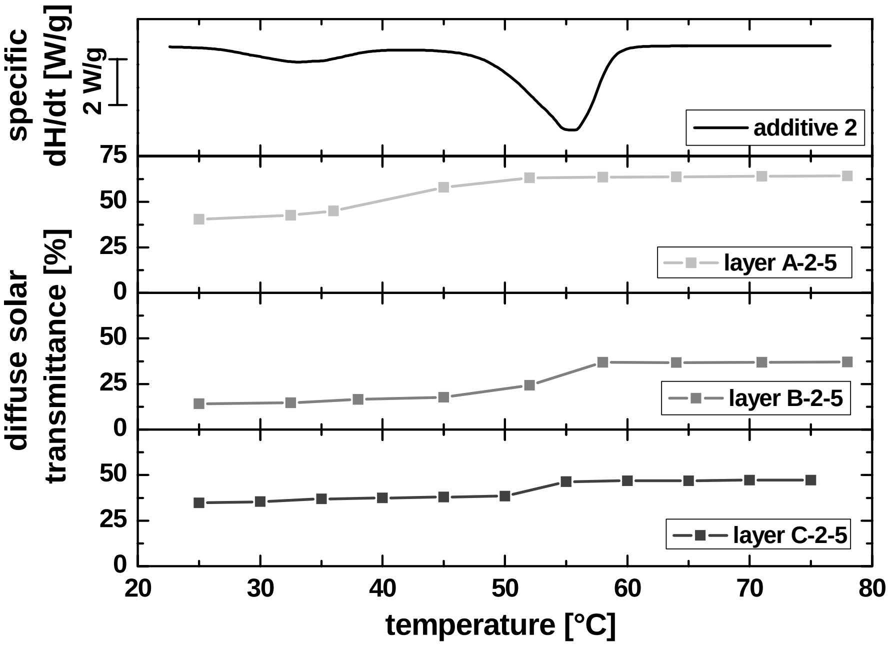


Fig. 3: Thermogram of additive 2 (top) and diffuse solar transmittance of thermotropic layers formulated with additive 2 as a function of temperature; top down: A-2-5, B-2-5, C-2-5.

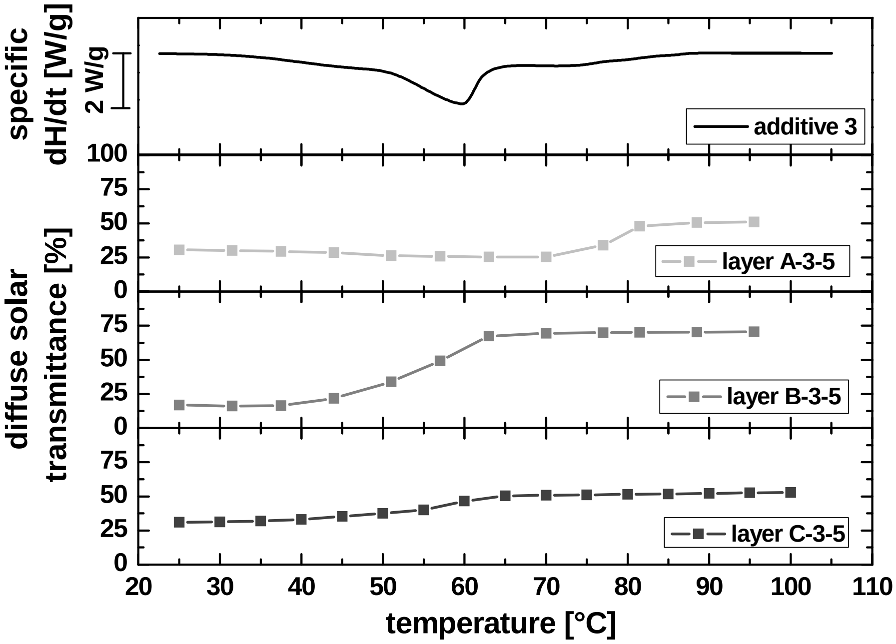


Fig. 4: Thermogram of additive 3 (top) and diffuse solar transmittance of thermotropic layers formulated with additive 3 as a function of temperature; top down: A-3-5, B-3-5, C-3-5.

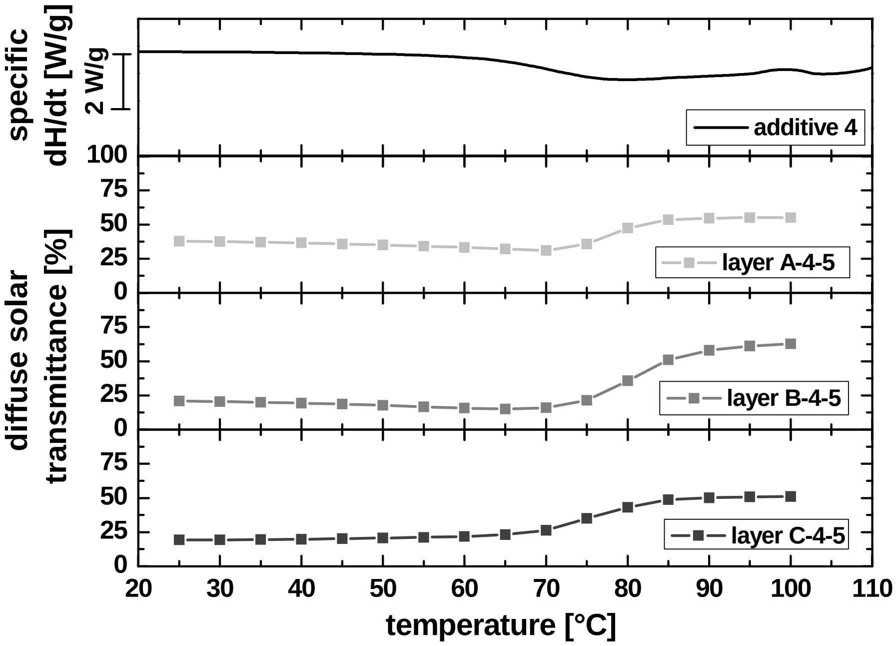


Fig. 5: Thermogram of additive 4 (top) and diffuse solar transmittance of thermotropic layers formulated with additive 4 as a function of temperature; top down: A-4-5, B-4-5, C-4-5.

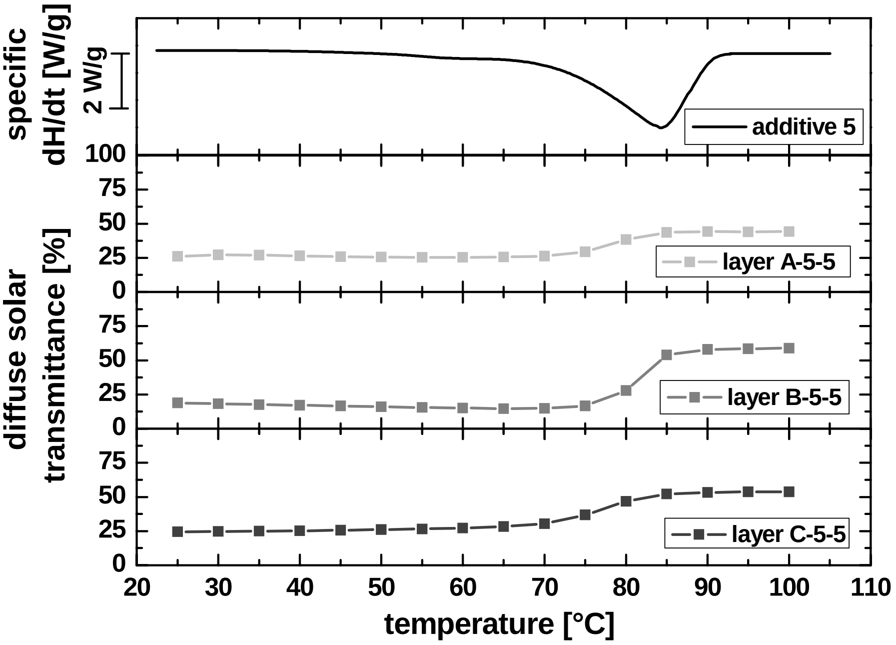


Fig. 6: Thermogram of additive 5 (top) and diffuse solar transmittance of thermotropic layers formulated with additive 5 as a function of temperature; top down: A-5-5, B-5-5, C-5-5.

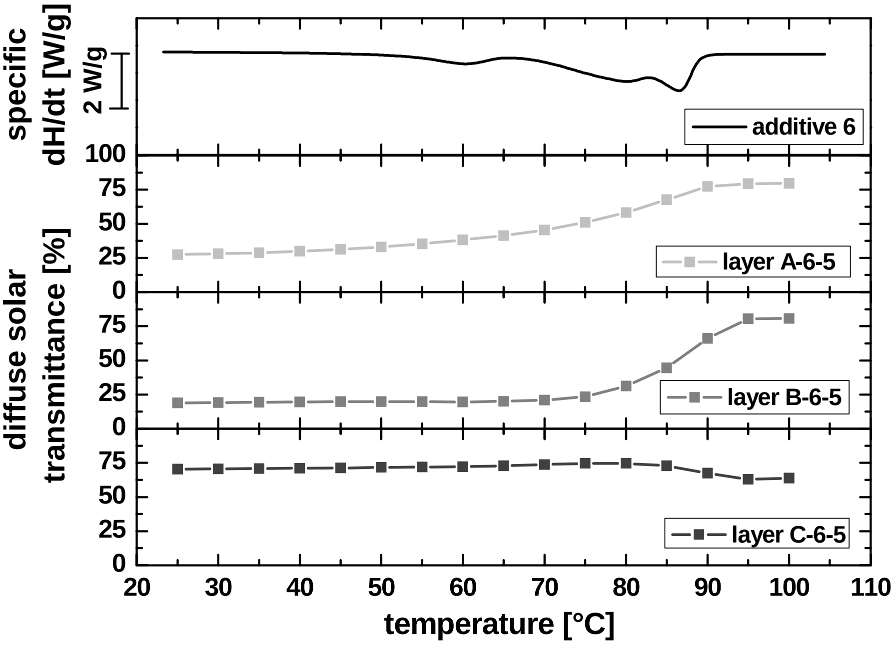


Fig. 7: Thermogram of additive 6 (top) and diffuse solar transmittance of thermotropic layers formulated with additive type 6 as a function of temperature; top down: A-6-5, B-6-5, C-6-5.

In general, upon heating the comparison of the layers switching characteristics with the additive's thermal transitions reveals a good correlation. This indicates that conclusions as to thermosensitivity of TSFD can be drawn from thermo-analytical measurements on thermotropic additives. Furthermore the relationships presented in Figs. 3 to 7 show that the switching temperature of the functional material can be tailored by selecting adequate additives.

4 Theoretical Modeling

4.1 Experimental background

The effect of selected thermotropic layers on maximum absorber temperatures in an all-polymeric flat-plate collector was evaluated by theoretical modeling applying a software generated by AEE-INTEC (Gleisdorf, AUT) (Solar, 1997-2006). This software provides a comprehensive theoretical mathematical description of flat-plate solar collector performance. A description of the model collector along with details as to ambient conditions is given in Wallner et al. (2008). For the present study a collector configuration with black absorber (solar absorbance α of 0.95, infrared emittance ε of 0.90) and a 10 mm twin-wall sheet glazing (thermal conductivity of material 0.20 W/(mK), solar absorbance 0, thermal emittance 0.90, thermal transmittance 0, refractive index 1.59) was chosen. The thermotropic layer as overheating protection device was attached either to the back side of the glazing (nomenclature: thermotropic glazing) or to the absorber (nomenclature: thermotropic absorber). As to the light transmission properties of the thermotropic layer the solar transmittance was determined by UV/Vis/NIR spectroscopy as a function of the temperature. For the functional film a thermal conductivity of 0.20 W/(mK), a solar absorbance of 0, a thermal transmittance of 0 and a thermal emittance of 0.90 was specified. The refractive index of the polymer is 1.50. Efficiency graphs were generated for a solar irradiation of 1000 W/m² and an ambient air temperature of 20°C.

4.2 Results and Discussion

In Figs. 8 and 9 the collector efficiency is plotted as a function of the absorber temperature for collectors without and with thermotropic overheating protection. Figure 8 illustrates efficiency graphs for the thermotropic layers A-5, C-4 and C-6 with an additive concentration of 5 m%. Both thermotropic glazing (top) and thermotropic absorber (bottom) are considered. Compared to the collector without overheating protection the application of thermotropic layers yields a shift of the overall collector efficiency to lower values. This can be ascribed to the hemispheric transmittance of the thermotropic layers ranging below 87% in the clear state. The decreased overall collector efficiency leads already to a reduction of the maximum absorber temperatures. Whereas for collectors without overheating protection a maximum absorber temperature of 158°C is obtained, even by the use of thermotropic layer A-5-5 that exhibits a moderate switching range of 8% the stagnation temperatures can be limited to ~145°C. Functional material C-4-5 with a reduction of transmittance by 10% limits stagnation temperatures to ~140°C. The thermotropic glazing yielding the best overheating protection (absorber temperatures of ~136°C) is material type C-6-5, that changes the solar transmittance by 14%. Compared to thermotropic glazing the application of thermotropic layers on the absorber causes a shift of the efficiency drop to lower temperatures.

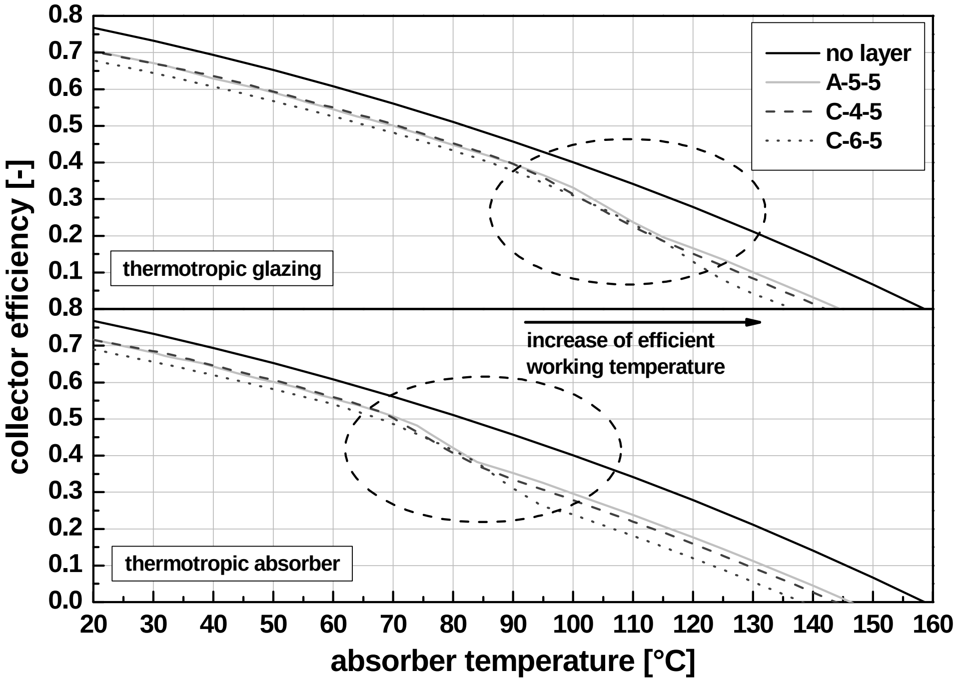


Fig. 8: Effect of thermotropic layers A-3-5, A-4-5, A-5-5, C-4-5, C-5-5, C-6-5 on collector efficiency and maximum absorber temperature of a solar collector with twin-wall sheet glazing and black absorber (α=0.95, ε=0.90) at a solar irradiation of 1000W/m² and an ambient temperature of 20°C.

Although as to their switching temperatures (70-80°C) the considered thermotropic layers should be theoretically suited for the application on the absorber (switching temperatures between 75 and 80°C required), to maximize the efficient working temperature range and to minimize stagnation temperatures the considered thermotropic layers have to be attached rather to the glazing than to the absorber. This effect can be attributed to the low switching ranges and the high transition range >10K of the produced thermotropic layers. This indicates that the positioning of thermotropic layers is primarily dependent on their switching range and the switching performance. The switching temperature is more important for the layer positioning if the reduction of the hemispheric transmittance exceeds 25% and the layer exhibits a rapid and steep switching process.

The effect of the thermotropic layer's additive concentration on the collector efficiency graphs is shown in Fig. 9. As thermotropic layers material types A-3 and C-6 were implemented. For these film types the strongest increase of the switching range by a variation of the additive concentration was ascertained. In general it is observable that with increasing additive concentration and thus decreased solar transmittance the overall collector efficiency in the clear state decreases. With thermotropic layers A-3-5 and A-3-7 stagnation temperatures can be limited to 141 and 135°C, respectively. The higher switching range of layer A-3-5 compared to layer A-3-7 is reflected in a steeper decrease of the collector efficiency in the transition range. It is observable that the layer with an additive concentration of 7 m% exhibits a lower switching temperature than the film formulated with an additive content of 5 m%. Due to the increase in additive concentration also molecules of this additive type are significant which contribute to the melting region around 60°C (see Fig. 4). For thermotropic layers based on resin type C and being formulated with additive type 6 no effect of the additive concentration on the switching temperature is detectable. The application of these thermotropic layers yields a reduction of maximum absorber temperatures by up to 29°C, as stagnation temperatures of 129 and 136°C are obtained for an additive concentration of 7 and 5 m%, respectively. A maximum operating temperature of 130°C would allow for the application of cost-efficient plastics as absorber materials. Nevertheless, further material development should focus on an increase of the collector efficiency in clear state and thus of the hemispheric solar transmittance. An increase of solar transmittance in clear state, however, has to be associated by an increase of the switching range. Otherwise maximum absorber temperatures exceed 130°C.

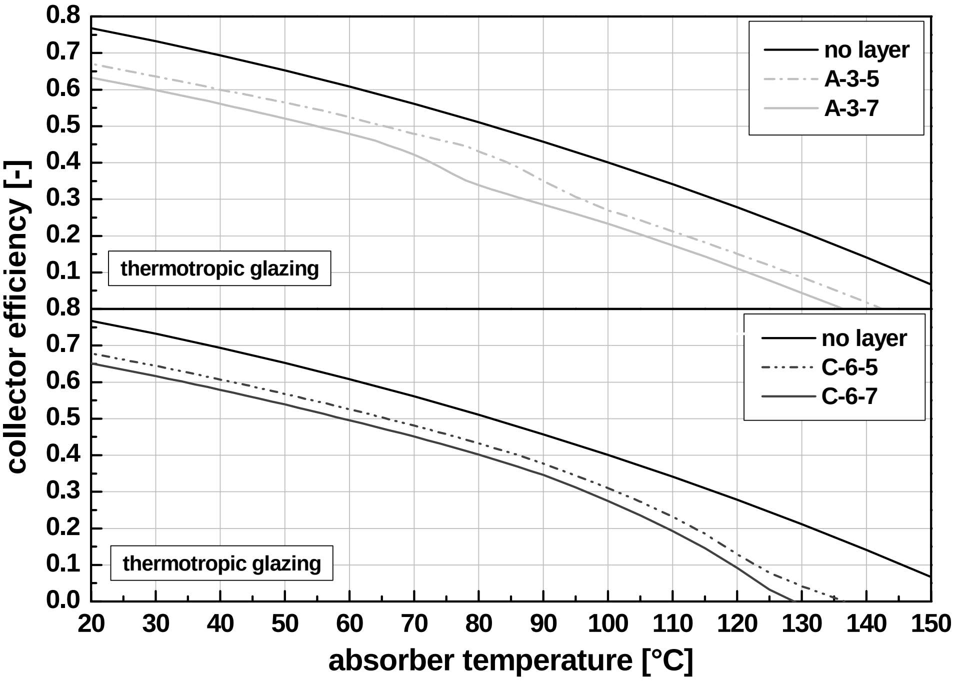


Fig. 9: Effect of formulated additive concentration of thermotropic layers A-3 and C-6 on collector efficiency and maximum absorber temperature of a solar collector with twin-wall sheet glazing and black absorber (α=0.95, ε=0.90) at a solar irradiation of 1000W/m² and an ambient temperature of 20°C.

5. Summary and Conclusion

In this paper the effect of resin and additive type on the light-shielding performance of TSFD with resin matrix was investigated. In clear state the thermotropic layers exhibited a hemispheric solar transmittance between 76 and 87%, with diffuse fractions ranging from 14 to 71%. The materials underwent the transition from the clear to the scattering state at temperatures between 40 and 80°C. For the investigated thermotropic layers transition temperature ranges between 10 and 25 K were recorded. Above the switching threshold the solar transmittance changes by 1 to 18% to values ranging between 62 and 85%, with diffuse fractions between 36 and 78%. The most efficient additive content of the considered thermotropic layers was found to be 5 m%. A stronger decrease of hemispheric solar transmittance was observed for thermotropic layers based on resin types which exhibit a higher cross-linking density and low chain mobility (high glass transition temperature). Thermotropic layers based on a resin with a wide-meshed network and low glass transition temperature were detected to exhibit the most distinct increases of diffuse solar transmittance above the switching threshold. The switching range of the thermotropic layers being formulated with non-polar additive types was found to increase with increasing molecular weight of the additives. The comparison of the additives thermal transitions with the switching performance of the thermotropic layer revealed a good correlation. This enables the development of thermotropic materials exhibiting tailor-made switching temperatures by selecting adequate additives.

The capability of selected thermotropic resins to prevent overheating of an all-polymeric solar collector was evaluated applying theoretical modeling. To maximize the efficient working temperature range and minimize stagnation temperatures the investigated layers were detected to be more appropriate for the use in the glazing than for the application on the absorber. Thermotropic layers were found to reduce the maximum absorber temperatures by 12 to 29°C to values between 129 and 146°C. Stagnation temperatures below 130°C would allow for the application of cost-efficient plastics as absorber materials. However, due to the low hemispheric transmittance of the thermotropic layers in the clear state overall collector efficiency is decreased. Thus further research should focus on the development of thermotropic resins with higher solar transmittance in the clear state associated by an increase of the switching range.

Acknowledgements

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH within the framework of the Non-K_{plus} Program.

This work is funded by the State Government of Styria, Department *Zukunftsfonds Steiermark*. ZUKUNFTSfonds STEIERMARK Das Land Steiermark

The authors wish to express their acknowledgements to Cytec Surface Specialties (Drogenbos, BEL), Sasol Germany GmbH (Hamburg, GER) and Chemson Polymer Additive AG (Arnoldstein, AUT), for providing the materials.

References

Bird, R.E., Hulstrom, R.L., 1983. Terrestrial solar spectral data sets. Solar Energy 30, 563-573.

Dabisch, W., 1978. Koerper mit reversibel veränderlicher temperaturabhängiger Lichtextinktion und Verfahren zur Herstellung des Koerpers. EP 0000868: 1978.

Hammami, A., Mehrotra, A.K., 1995. Thermal behaviour of polymorphic n-alkanes: effect of cooling rate on major transition temperatures, Fuel 74, 96-101.

Khan, A., Brunger, A., 1997. Thermal Protection of Flat Plate Solar Collectors Using Thermotropic Glazings. In Proceedings 23rd Annual Conference of the Solar Energy Society of Canada Inc: Implementing Sustainable Energy in a Changing World, Vancouver, Canada, pp. 119-124.

Meyer, G., Matthai, M., Auge, J., Lindow, H., 2005. Crystallisation processes and hardness of paraffin waxes characterised by DSC, ultrasonic, x-ray and needle penetration measurements. SÖFW-journal 131, 51-58.

Nitz, P., 1999. Optische Modellierung und Vermessung thermotroper Systeme. PhD Thesis, Fakultät fuer Physik, Albert-Ludwigs-Universität Freiburg im Breisgau.

Nitz, P., Hartwig, H., 2005. Solar control with thermotropic layers. Solar Energy 79, 573-582.

Resch, K., Hausner, R., Wallner, G.M., 2007. All polymeric flat-plate collector – potential of thermotropic layers to prevent overheating. In Proceedings of ISES Solar World Congress, Beijing, China, pp. 561-565.

Resch, K., Wallner, G.M., 2007. Thermotropic resin systems: relationships between formulation parameters, material structure and optical properties. In Proceedings of ISES Solar World Congress, Beijing, China, pp. 541-545

Resch, K., Wallner, G.M., Lang, R.W., 2008. Spectroscopic investigations of phase- separated thermotropic layers based on UV cured acrylate resins. Macromolecular Symposia 265, 49-60.

Resch, K., Wallner, G.M., 2008. Thermotropic layers for flat-plate collectors – a review of various concepts for overheating protection with polymeric materials. Submitted to Solar Energy Materials and Solar Cells.

Riegler, H., Koehler, R., 2007. How pre-melting on surrounding interfaces broadens solid-liquid phase transitions. Nature Physics 3, 890-894.

Sakai, H., 1996. Surface-induced melting of small particles. Surface Science 351, 285-291.

Seeboth, A., Schneider, J., Patzak, A., 2000. Materials for intelligent sun protecting glazing. Solar Energy Materials and Solar Cells 60, 263-277.

SOLAR, 1997-2006. Wärme- und stroemungstechnische Berechnungen, Unterprogramm: Theoretischer Kollektor. AEE INTEC, Gleisdorf, AUT.

Wallner, G.M., Resch, K., Hausner, R., (2008). Property and performance requirements for thermotropic layers to prevent overheating in an all polymeric flat-plate collector. Solar Energy Materials and Solar Cells 92, 614-620.

6 Conclusions and Future Work

6.1 Contributions of this Dissertation

This dissertation and the papers presented herein provide the basic knowledge on the development of polymeric thermotropic materials for overheating protection of solar collectors. In the following, the substantial contributions are summarized with respect to the objectives defined for this dissertation.

The evaluation and strength-weakness analysis of existing thermotropic layers produced from polymeric materials concerning their applicability in solar collectors included thermotropic hydrogels, thermotropic polymer blends, and thermotropic systems with fixed domains (TSFD). It was found that for solar collector applications, thermotropic systems designed so far have to be adapted and optimized, especially regarding their switching temperatures and long-term stability. Distinct advantages such as the easy adjustment of the switching threshold, high possible operating temperatures, high reversibility, and low hysteresis favor the use of TSFD over thermotropic hydrogels and thermotropic polymer blends for overheating protection purposes in a solar collector.

In TSFD, scattering particles (also referred to as additives), which exhibit a sudden change of refractive index with temperature, are statically embedded in a matrix material (mostly a duromer resin). At low temperatures the layer is translucent, as the refractive indices of matrix and domain are almost equal. The differing temperature dependence of the refractive index for the components above the switching threshold causes the thermotropic film to turn opaque. The polymer physics based development and design of thermotropic prototype-layers for solar collector applications described in this dissertation included first of all the establishment of a methodological approach for the determination of cross-linking parameters (curing rate, degree of cure) and the glass transition temperature of the matrix material relevant for the production of TSFD. Investigations were done using exemplarily a UV-curable urethane acrylate resin. It was shown that applying Dielectric Analysis (DEA), Attenuated Total Reflectance spectroscopy (ATR) and Dynamic Mechanical Analysis (DMA) relevant performance properties of a matrix material can be derived. To perform a systematic investigation for the preparation of thermotropic prototype-layers, three UV-curable resin materials with differing chemical backbone were selected. The matrix oligomers included a polyester acrylate, a urethane acrylate and an epoxy acrylate. In order to meet the requirements as to overheating protection of a solar thermal collector, six thermotropic additives with appropriate thermal transition temperatures were chosen. Paraffin waxes and esters of an alcohol were considered. Numerous prototype-layers were prepared by variation of base resin and additive type. Additives were incorporated into the resin in concentrations of 5 and 7 m%.

A comprehensive characterization of thermotropic prototype-layers as to relevant morphological parameters and performance properties showed at first that the layers exhibited a hemispheric solar transmittance between 76 and 87% in the clear state, with diffuse fractions ranging from 14 to 71%. The switching from the clear to the scattering state occurred at temperatures between 40 and 80°C. Transition temperature ranges between 10 and 25 K were recorded. Above the switching threshold the hemispheric solar transmittance changed to values ranging between 62 and 85%, with diffuse fractions between 36 and 78%. The optical properties of the thermotropic layers in the clear and the scattering state were observed to depend significantly on the differences in the refractive indices of the matrix and additive, additive concentration, and distribution as well as on scattering domain size. Pronounced differences in refractive index between matrix and additive (>0.04) above the switching temperature were detected to be advantageous for the light-shielding efficiency of the layers. The most efficient additive concentration for the considered thermotropic layers was found to be 5 m%. A uniform additive distribution across the film thickness was ascertained to be beneficial for the reflectance efficiency in the scattering state. Relationships between the changes in hemispheric and diffuse solar transmittance of the thermotropic layers above the switching threshold and scattering domain size and shape were established. Thermotropic layers formulated with additive types exhibiting a short chain length displayed roughly spherical scattering particles with dimensions between 0.5 and 3 µm and a moderate reduction in hemispheric solar transmittance along with a significant increase of diffuse solar transmittance. Additives types with long-chain molecules developed anisotropic scattering domains resembling contorted disks with a diameter below 50 µm and a thickness between 100 to 400 nm. The obtained anisotropic scattering features were detected to yield improved light-shielding properties compared to spherical particles with dimensions ranging from 0.5 to 3 µm.

Furthermore, this dissertation included the establishment of structure-property relationships between the performance properties and the inner material structure and formulation parameters of thermotropic prototype-layers to provide a basis for further research work and a systematic material optimization. A stronger decrease of the hemispheric solar transmittance in the scattering state was observable for thermotropic layers based on resin types which exhibit a higher cross-linking density and low chain mobility (high glass transition temperature). Thermotropic layers based on a resin with a wide-meshed network and low glass transition temperature displayed a moderate reduction in solar transmittance along with the most distinct increases of diffuse solar transmittance above the switching threshold. The switching range of the thermotropic layers being formulated with non-polar additive types was shown to increase with increasing molecular mass of the additives. An excellent correlation between the thermal transitions of the additives and the switching characteristics of the thermotropic layer was ascertained. Hence, the switching temperature and transition temperature ranges of TSFD can be tailored by selecting adequate additives.

Finally, investigations concerning the effect of thermotropic prototype-layers on the efficiency of an all-polymeric flat-plate collector were carried out. The overall collector efficiency in the clear state was found to decrease when thermotropic layers are applied. To maximize the efficient working temperature range and to minimize stagnation temperatures, the investigated layers were detected to be more appropriate for the use in the glazing than for the application on the absorber. The thermotropic layers investigated were found to reduce the maximum black absorber temperatures to values between 129 and 146°C.

6.2 Open Issues and Suggestions for Future Work

Within this dissertation, TSFD were evaluated from a polymer physics and materials science point of view. It was shown that the materials investigated are not yet optimal for overheating protection of a solar collector. However, some major routes for further research to achieve better results became appppparent. In the following, the most important open issues which should be addressed in future work are described.

To control stagnation temperatures in solar collectors and to allow for the application of cost-efficient plastics as absorber materials, thermotropic layers showing a reduction of the solar transmittance of at least 25% above the switching threshold are required. For the thermotropic prototype-layers prepared within the presented dissertation a decrease of the solar transmittance by maximum 18% was ascertained. Hence, the light-shielding efficiency of the thermotropic layers still has to be improved. The moderate reduction of the solar transmittance can be attributed primarily to inappropriate scattering domain size and shape, as the change in refractive index was found to be effectual. Optimum reflectance efficiency is obtained with spherical scattering particles that exhibit diameters between 200 and 400 nm. In TSFD prepared and investigated so far the scattering domains were anisotropic and/or exhibited sizes which are inappropriate for high reflectance efficiency in the solar spectral range. The optimization of the primary performance property of the thermotropic materials, i.e. reduction in solar transmittance, thus requires the adjustment of the scattering domain size and shape. This could be achieved by the incorporation of scattering domains, which already possess the necessary shape and sizes. This may be resolved by producers of thermotropic additives. Conversely, the scattering particle size and distribution is dependent on the matrix material. The selection of adequate resin types may therefore also favor the development of appropriate scattering domains.

In addition to the adjustment of the reduction in solar transmittance, the maintenance of the light-shielding capability of the thermotropic layer for a long time is of importance. For this purpose, the incorporated additive must be fixed to prevent migration if the layer is exposed to elevated temperatures for prolonged periods. In this regard the chemical backbone and the cross-linking characteristics of the resin material play a key-role. Hence, the selection of appropriate resin formulations is of special relevance.

For a systematic optimization of TSFD the combined knowledge of resin manufacturers, producers of thermotropic additives, and polymer scientists is required. A close cooperation between these specialists should be aimed for in a future study to adapt layer properties for overheating protection properties of solar collectors. In this regard also specific focus should be given to adequate temperature stability and durability of the layers. Further material development and optimization should be done based on the findings and results concerning interrelationships between material formulation, morphological characteristics and performance properties of TSFD provided within this dissertation.

From the author’s point of view, the availability of adequate thermotropic layers and thus of an appropriate overheating protection can revolutionize the solar thermal collector market. It allows for the application of cost-efficient plastics as materials for the absorber and for various other components of a solar collector. The use of polymers in solar components and systems yields cost reduction, functional improvements and more design freedom. This is serving to make solar thermal systems more attractive to architects and end-users and thus may act to increase the use of renewable energy for low-temperature heating purposes – a big step towards the development of a sustainable energy future.

APPENDIX

List of Publications by the Author

Publications Related to this Dissertation

Papers in Refereed Journals

K. Resch, G.M. Wallner, R.W. Lang (2008). Cross-linking behavior of UV-curable acrylate resins, in press for Journal of Plastics Technology.

K. Resch, G.M. Wallner (2008). Thermotropic layers for flat-plate collectors – A review of various concepts for overheating protection with polymeric materials, in press for Solar Energy Materials and Solar Cells.

K. Resch, G.M. Wallner, R.W. Lang (2008). Spectroscopic investigations of phase-separated thermotropic layers based on UV cured acrylate resins, Macromolecular Symposia **265**, 49-60.

G.M. Wallner, K. Resch, R. Hausner (2008). Property and performance requirements for thermotropic layers to prevent overheating in an all polymeric flat-plate collector, Solar Energy Materials & Solar Cells **92**, 614-620.

Papers Submitted to Refereed Journals

K. Resch, G.M. Wallner (2008). Material structure and morphology of phase-separated thermotropic layers based on UV cured acrylate resins (submitted to: Polymers for Advanced Technologies*)*

K. Resch, G.M. Wallner, R. Hausner (2008), Phase separated thermotropic layers based on UV cured acrylate resins – structure-property relationships (submitted to: Solar Energy)

Papers in Conference Proceedings

K. Resch, R. Hausner, G.M. Wallner (2008). Modeling of an all polymeric flat-plate collector with thermotropic overheating protection, in Proceedings of EUROSUN 2008 - 1st International Conference on Solar Heating, Cooling and Buildings, Lisbon, PT, October 7-10, No. 361.

K. Resch, G.M. Wallner (2008). Thermotropic materials for overheating protection of solar collectors, in Proceedings of EUROSUN 2008 - 1st International Conference on Solar Heating, Cooling and Buildings, Lisbon, PT, October 7-10, No. 360.

*K. Resch, J. Fischer, A. We*ber, G.M. Wallner (2008). Overheating protection with thermotropic resin systems: Effect of material structure and morphology on light-shielding efficiency, in Proceedings of EUROSUN 2008 - 1st International Conference on Solar Heating, Cooling and Buildings, Lisbon, PT, October 7-10, No. 359.

G.M. Wallner, R. Hausner, K. Resch, H. Schobermayr (2008). Development of polymeric collectors with integrated overheating protection, in Proceedings of Gleisdorf Solar 2008, Gleisdorf, AT, September 3-5, 85-90.

K. Resch, G.M. Wallner (2008). Entwicklung und Charakterisierung thermotroper Materialien, in Proceedings of 2nd Leobener Symposium Polymeric Solar Materials, Leoben, AT, February 7-8, XIV–1-11.

R. Hausner, K. Resch, G.M. Wallner (2008). Modellierung von Kunststoffkollektoren mit Überhitzungsschutz, in Proceedings of 2nd Leobener Symposium Polymeric Solar Materials, Leoben, AT, February 7-8, IV–1-8.

K. Resch, G.M. Wallner (2007). Thermotropic resin systems: Relationships between formulation parameters, material structure and optical properties, in Proceedings of ISES Solar World Congress 2007, Beijing, CN, September 18-21, 541-545.

K. Resch, R. Hausner, G. Wallner (2007). All polymeric flat-plate collector – potential of thermotropic layers to prevent overheating, in Proceedings of ISES Solar World Congress 2007, Beijing, CN, September 18-21, 561-565.

R. Hausner, G. Wallner, K. Resch (2007). Solarthermische Kunststoffkollektoren mit integriertem Überhitzungsschutz, in Proceedings of 17. Symposium Thermische Solarenergie OTTI, Staffelstein, DE, September 18-21, 1-6.

G.M. Wallner, K. Resch, R. Hausner (2006). Solarthermische Kunststoffkollektoren mit integriertem Überhitzungsschutz, in Proceedings of Gleisdorf Solar 2006, Gleisdorf, AT, September 6-8, 105-114.

Oral Presentations (presenting author underlined)

K. Resch, G.M. Wallner (2008). Effect of morphology on the light-shielding efficiency of thermotropic systems with fixed domains, IEA Task 39 Workshop, Lisbon, PT, October 13-15.

K. Resch, R. Hausner, G.M. Wallner (2008). Modeling of an all polymeric flat-plate collector with thermotropic overheating protection, EUROSUN 2008 - 1st International Conference on Solar Heating, Cooling and Buildings, Lisbon, PT, October 7-10.

K. Resch, G.M. Wallner (2008). Thermotropic materials for overheating protection of solar collectors, EUROSUN 2008 - 1st International Conference on Solar Heating, Cooling and Buildings, Lisbon, PT, October 7-10.

K. Resch, P. Nitz, H.R. Wilson (2008). Optical modeling of thermotropic systems, IEA Task 39 Workshop, Oslo, NO, April 28-30.

K. Resch, G.M. Wallner (2008). Crosslinking reactions and network structure in UV-curable acrylate resins, 1st Joint Austrian & Slovenian Polymer Meeting ASPM 2008 and 9th Austrian Polymer Meeting, Graz, AT, March 26-28.

K. Resch, G.M. Wallner (2008). Entwicklung und Charakterisierung thermotroper Materialien, 2nd Leobener Symposium Polymeric Solar Materials, Leoben, AT, February 7-8.

K. Resch, G.M. Wallner (2007). Polymeric materials for solar thermal applications, IEA Netzwerktreffen, Wien, AT, October 22.

K. Resch, G.M. Wallner (2007). Review on thermotropic polymers, IEA Task 39 Workshop, Blumau, AT, September 26-27.

K. Resch, R. Hausner, G. Wallner (2007). All polymeric flat-plate collector - potential of thermotropic layers to prevent overheating, ISES Solar World Congress 2007, Beijing, CN, September 18-21.

K. Resch, G.M. Wallner (2007). Thermotropic resin systems: Relationships between formulation parameters, material structure and optical properties, ISES Solar World Congress 2007, Beijing, CN, September 18-21.

K. Resch, G.M. Wallner (2007). Spectroscopic characterization of thermotropic resins, 17th European Symposium on Polymer Spectroscopy, Seggauberg, AT, September 10-12.

K. Resch, G. Oreski (2007). Polymere für die Solartechnik – Struktur-Eigenschafts-Korrelationen, 2. internes wissenschaftliches Symposium der Polymer Competence Center Leoben GmbH, Leoben, AT, June 15.

K. Resch, G.M. Wallner (2007). Characterization of thermotropic resin systems, IEA Task 39 Workshop, Aveiro, PT, May 3-4.

K. Resch, G.M. Wallner, R. Hausner (2006). Kunststoffkollektoren mit integriertem Überhitzungsschutz, Boardsitzung der Polymer Competence Center Leoben GmbH, Leoben, AT, November 15.

Posters

K. Resch, J. Fischer, A. Weber, G.M. Wallner (2008). Overheating protection with thermotropic resin systems: Effect of material structure and morphology on light-shielding efficiency, presented at EUROSUN 2008 - 1st International Conference on Solar Heating, Cooling and Buildings, Lisbon, PT, October 7-10.

Publications beyond this Dissertation

Papers in Refereed Journals

K. Resch, G.M. Wallner, C. Teichert, M. Gahleitner (2007). Highly transparent polypropylene cast films: Relationships between optical properties, additives, and surface structure, Polymer Engineering and Science **47**, 1021-1032.

K. Resch, G.M. Wallner, C. Teichert, G. Maier, M. Gahleitner (2006). Optical properties of highly transparent Polypropylene Cast Films: Influence of Material Structure, Additives and Processing Conditions, Polymer Engineering and Science **46**, 520-531.

G.M. Wallner, K. Resch, C. Teichert, W. Binder, M. Gahleitner (2006). Effect of material structure and additives on the optical properties of PP cast films, Journal Monatshefte für Chemie / Chemical Monthly **137**, 887-897.

G.M. Wallner, K. Resch, G. Hlawacek, C. Teichert, G. Maier, W. Binder, M. Gahleitner (2004). Correlation between material structure, processing conditions and optical properties of PP cast films, in Proceedings of the 62nd Annual Technical Conference & Exhibition ANTEC 2004, Chicago, IL, US, May 16-20, Vol. I, 1096-1100.

Oral Presentations (presenting author underlined)

K. Resch, G.M. Wallner, M. Mikl, C. Teichert, M. Gahleitner (2006). Highly transparent polypropylene cast films: Polymerphysical characterization and structure-property correlations, 8th Austrian Polymer Meeting, Linz, AT, September 18-20.

K. Resch (2005). Spectrally selective polymer films, Polymer Competence Center Leoben GmbH 4Y Evaluation, Leoben, AT, Oktober 19-20.

K. Resch, G.M. Wallner, C. Teichert (2005). Optical Properties of highly transparent polypropylene cast films: Influence of material structure, additives and processing conditions, 7th Austrian Polymer Meeting, Graz, AT, July 4-6.

K. Resch, G.M. Wallner (2004). Correlation between material structure, processing conditions and optical properties of PP cast films, SPE-Annual Technical Conference, Chicago, IL, US, May 16-18.

Posters

K. Resch, G.M. Wallner, C. Teichert, M. Gahleitner and W. Binder (2003). Relationships between the surface structure and the optical properties of PP cast films, presented at 6th Austrian Polymer Meeting, Vienna, AT, September 15-17.

K. Resch, G. Wallner, G. Hlawacek, C. Teichert, M. Gahleitner, W. Binder (2005). Nanometer scale characterization of polypropylene cast film surfaces, presented at 6th Workshop Rasterkraftmikroskopie in der Werkstoffwissenschaft, Erlangen, DE, February 17-18.

M. Mikl, K. Resch, G.M. Wallner, C. Teichert (2006). Topographical characterization of polypropylene cast films by scanning probe and laser confocal microscopy, presented at 8th Austrian Polymer Meeting, Linz, AT, September 20-22.