Available online at www.sciencedirect.com
ScienceDirect
Solar Energy 110 (2014) 420–426
SOLAR ENERGY
www.elsevier.com/locate/solener

Black-pigmented polypropylene materials for solar thermal absorbers – Effect of carbon black concentration on morphology and performance properties

M. Povacz*, G.M. Wallner, R.W. Lang

Institute of Polymeric Materials and Testing, Johannes Kepler University Linz, Austria

Received 2 June 2014; accepted 17 September 2014
Available online 17 October 2014

Communicated by: Associate Editor Yogi Goswami

Abstract

Black-pigmented polyolefin compounds are widely used for unglazed collectors and recently also for glazed flat-plate collectors with overheating protection. In this paper the effects of pigment concentration (carbon black (CB) – masterbatch) on morphology and performance properties of a polypropylene grade for elevated temperature applications (PP-RCT) are investigated. Compounds with varying black pigment concentrations (from 0.1 to 1.0 wt.%) were prepared and moulded to 2 mm thick sheets. Morphological characteristics, optical and mechanical properties, as well as long-term properties were characterized on specimen level by optical microscopy, Differential Scanning Calorimetry (DSC), UV/Vis/NIR- and IR-spectrometry and tensile testing. The investigated black compounds exhibited integral solar absorbance values of about 95% and integral infrared emittance values from 93% to 95%. Hence, the effect of black pigment concentration on the solar- and infrared-optical properties was small. Regarding the mechanical properties, the elastic modulus and the ultimate properties were slightly affected by the black pigment content. A more pronounced effect was deduced after long-term exposure in hot air at 135 °C. With increasing carbon black concentration a significant reduction of the embrittlement time from approximately 4000 h to 3200 h was obtained.

Keywords: Solar thermal applications; Polypropylene; Carbon black; Aging behaviour

1. Introduction

Polymeric materials offer a cost reduction potential for solar thermal applications due to processing advantages, design freedom and improved performance specifications (Wallner and Lang, 2005; Kahlen et al., 2010a, b). The usage of polymers in solar thermal applications is no longer limited to casing, glazing and sealing materials. Engineering and high-performance polymers are already used to replace copper and aluminum as absorber materials (e.g., in the Aventa® collector). Kahlen et al. (2010a, b) investigated the applicability of commodity plastics for solar thermal absorbers and deduced that especially polypropylene (PP) would be a promising material candidate for collectors with adequate overheating control used in northern climates (i.e., absorber temperature below 140 °C). The research work of Kahlen et al. (2010a, b) was confined to investigations on unpigmented polyolefin grades. Regarding the aging behaviour, exposure test in air at 140 °C up to 500 h and in water at 80 °C up to 16,000 h were carried out. For the unpigmented PP grades no premature failure was obtained.

* Corresponding author. Tel.: +43 (0) 732 2468 6621.
E-mail address: markus.povacz@jku.at (M. Povacz).

http://dx.doi.org/10.1016/j.solener.2014.09.024
0038-092X/

According to the classification of Levinson et al., 2005 and several pigment handbooks (e.g. Buxbaum, 1998; Mayer, 1991), carbon black belongs to the class of “hot” pigments, associated with high absorbance of the overall solar radiation range. Hence, carbon black is a promising and widely used pigment for solar thermal applications. Commodity plastics such as polyethylene (PE) and polypropylene (PP) with adequate carbon black pigmentation are already used for swimming pool absorbers (e.g. FAFCO® 200 and 500 series collectors), and recently they are more and more used in glazed collectors (e.g. ecoFLARE® collector produced by Magen Eco Energy) with appropriate overheating protection (Meir et al., 2012).

Nevertheless, investigations regarding the influence of carbon black on the aging behaviour of polyolefins are quite scarce (Allen et al., 1998; Horrocks et al., 1999). Jakab and Blazsó (2002) investigated the effect of carbon black on the thermal decomposition of vinyl polymers. A major result of their work was, that the decomposition of PP can be promoted by carbon black. An extension of the investigations using various types of carbon blacks revealed that the aging behaviour depends on the volatile content of the carbon blacks (Jakab and Omastová, 2005).

In a previous paper (Kurzböck et al., 2012) various black-pigmented polypropylene grades were evaluated. It was shown that PP-RCT grades with carbon nanotubes lack of fine pigment distribution. For various carbon black based grades with black pigment concentrations of about 1.5 wt.% remarkable performance properties were deduced. The main objective of this paper is to investigate carbon black pigmented PP-RCT compounds for solar thermal absorbers with black pigment concentration below 1.5 wt.%. By systematic variation of the carbon black concentration optimum pigment loadings for absorber materials should be deduced. Regarding the morphological features and the performance properties, special emphasis should be given to the quality of black particle distribution, semi-crystalline morphology, optical and mechanical short-term properties and long-term behaviour in hot air environment. More comprehensive aging investigations considering various specimen types and different application-relevant service conditions (e.g. also in hot heat carrier fluid) are currently carried out and will be published in subsequent papers.

2. Experimental

2.1. Materials

The β-nucleated polypropylene random copolymer (PP-RCT) chosen for this work is a grade for elevated temperature applications with a melt flow rate of 0.25 g/10 min (230 °C/2.16 kg) provided by Borealis Polyolefine GmbH (Linz, Austria). In contrast to previous work (Kurzböck et al., 2012) commercially available masterbatch based carbon black pigments with a primary pigment size of 60 nm were used (provided by Cabot Corporation, Boston, USA). Five different compounds with carbon black concentrations from 0.1 to 1.0 wt.% and a combination of phenolic and phosphite stabilizers were prepared.

To produce compounds with such low carbon black contents a two-step compounding process was used. First, the carbon black masterbatch with 50 wt.% carbon black content was compounded on a twin-screw extruder (Type: Prism TSE 24 HC; Thermo Fisher Scientific Inc., Waltham, USA) to grades with 1.5 wt.% carbon black. To provide best blend homogeneity the masterbatch flow was controlled through a cascade chamber. The screw speed was 400 rpm. In the second compounding step the concentrations were further reduced to values ranging from 0.1 to 1.0 wt.% carbon black. The pelletized compounds were injection-moulded into 3 mm thick plates. To obtain a homogeneous compound without flow and strain induced orientations, the injection-moulded plates were furthermore compression-moulded into 2 mm thick plaques. Unpigmented PP-RCT granules were similarly processed to receive reference specimens with the same thermo-mechanical history.

Tensile test specimens of the 5A type (ISO 527-2/5A) with an overall length of 75 mm were machined with a puncher. To derive detailed information on the pigment dispersion of the compounds and the effects on the mechanical and optical properties, micro-sized 50 and 100 μm thick film-specimens with a width of 20 mm and a length of 200 mm were automatically sliced on a CNC-machine (Wallner et al., 2013).

2.2. Characterization methods

Various analytical, optical, mechanical and aging characterization methods were chosen. Optical light microscopy in transmitted light mode was applied to check the dispersion quality of the masterbatch based carbon black pigmentation. Micro-sized specimens (i.e., slices with 50 μm thickness) were probed using a BX 61 microscope (Olympus Austria GmbH; Vienna, Austria) with 5×, 20× and 50× objectives in transmitting mode. The thermal transitions of the black pigmented plates were characterized by Differential Scanning Calorimetry (DSC), using a Perkin Elmer DSC 4000 (Perkin Elmer GmbH; Rodgau, Germany). At least 3 samples with mass of 0.8–1.2 mg were taken from sliced specimen and placed in 30 μl aluminium pans with perforated lids. DSC runs were performed with heating/cooling rates of 10 K min^{-1} under static air purge. Melting behaviour and β-phase content were determined from the 2nd heat-up thermogram according to Patent EP 0682066B2 (Bernreiter and Wolfschwenger, 2002). To analyse the morphology ratio the β- and α- peaks were evaluated and correlated. The results of the DSC-based method were supported and validated with wide angle X-ray scattering (WAXS) measurements done by Borealis Polyolefine GmbH, Linz.

The solar-optical properties of 2 mm thick plates were characterised using a Perkin Elmer Lambda 950 Ulbricht sphere spectrophotometer (Perkin Elmer GmbH; Rodgau; Germany). The diameter of the Spectralon Ulbricht sphere was 150 mm. Hemispherical absorbance values were derived from measured normal-hemispherical transmittance and reflectance spectra. The spectral data were weighted and integrated in steps of 5 nm by the AM 1.5 global solar irradiance source function (Bird et al., 1983). For the characterization of the heat radiation properties a Fourier Transform Infrared (FTIR) spectrometer (Perkin Elmer Spectrum 100 spectrometer) equipped with a gold coated Ulbricht sphere with a diameter of 100 mm was used. Normal-normal transmittance and reflectance spectra were recorded in the wavenumber range from 4000 to 700 cm^{-1} at a resolution of 2 cm^{-1} and an average of 128 scans. Integral infrared emittance values were obtained by weighting the measured data with black body functions for temperatures at 100 °C.

Mechanical properties were obtained by tensile testing of 5A multi-purpose specimens on a screw-driven universal testing machine (Type: Zwick Line Z5.0; Zwick GmbH & Co. KG; Ulm, Germany) according to DIN EN ISO 527-2 (1996). The initial clamping length was 50 mm, the test speed was 50 mm/min. For each series 5 specimens were tested at ambient temperature. The stress–strain curves were evaluated as to the Young's modulus, E_T, the yield stress, σ_Y, and the strain-at-break, ε_B. Small deformations were determined applying a multi-extensometer.

Regarding long-term properties micro-sized specimen (i.e. slices with 100 μm thickness) were exposed in a heating oven (Type: Binder FED 53; Binder GmbH; Tuttlingen, Germany) to hot air at 135 °C for up to 4000 h. After hot air exposure the specimen were characterized by Differential Scanning Calorimetry (DSC) and tensile testing (Type: Zwick Line Z2.5; Zwick GmbH & Co. KG; Ulm, Germany) at ambient temperature.

3. Results

3.1. Morphological characteristics and thermal transitions

In Fig. 1 optical micrograph images of 50 μm thin slices of the compression moulded compounds PP-RCT with 0.10, 0.25 and 1.00 wt.% carbon black are displayed. For the black pigmented compounds a fine dispersion of carbon black was detected. Small agglomerates with a diameter of 0.5 μm were dominating. With increasing concentration, the dispersion of carbon black is homogeneous and the visible agglomerates are below 1 μm (see Fig. 1c).

Representative DSC thermograms taken from the second heating run are depicted in Fig. 2. The unpigmented reference sample PP-RCT (orange curve) exhibited a double melting peak, which is characteristic for beta-nucleated polypropylene. The melting peak temperatures for the hexagonal β-crystallites and the monoclinic α-crystallites were obtained at 137 °C and 151 °C, respectively. Carbon black pigmentation lowers the melting temperatures of the PP-RCT compounds for about two degrees. The oxidation temperature of the reference specimen without carbon black was at 272 °C and slightly decreased for the pigmented compounds to 268 °C (Fig. 2b).

For the unpigmented reference material a β-phase content of 72% and 81% was obtained by DSC and WAXS, respectively. Concerning the pigmented PP-RCT grades, DSC measurements revealed that the incorporation of low amounts of carbon black pigments into the polypropylene random-copolymer matrix does not affect the β-phase content.

3.2. Solar and infrared optical properties

Fig. 3 illustrates the normal hemispherical reflectance spectra of the PP plaques with varying black pigment concentrations over the solar and infrared wavelength range. The reflectance spectra of the grades with varying carbon black content were comparable. Slight differences were obtained in the UV range (250–380 nm), in the NIR range (1000–2500 nm) and in the infrared wavelength range (2500–14285 nm). Compounds with the lowest carbon black concentration (0.1 wt.%) revealed a slightly lower reflectance in the overall wavelength range. By integration over the solar wavelength range integral solar reflectance values ranging from 4.8% to 4.9% were obtained. The reflectance in the heat radiation range was about 4.3%.

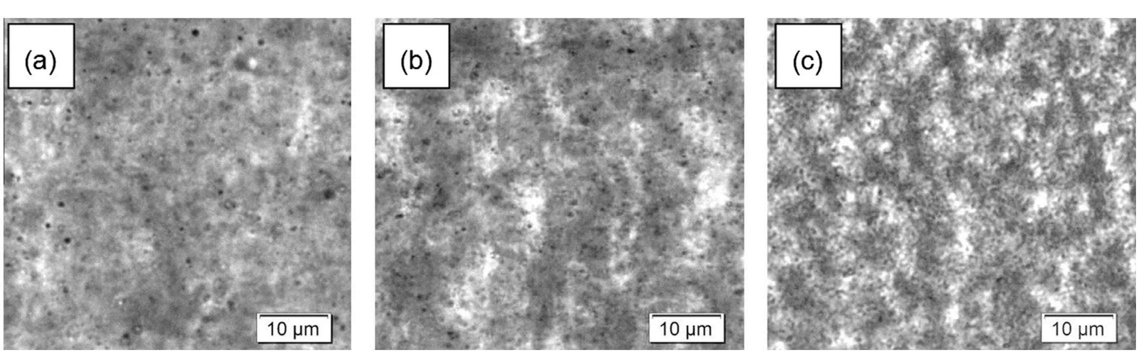

Fig. 1. Optical micrograph images of 50 μm thin slices of compression moulded PP-RCT compounds with (a) 0.10, (b) 0.25 and (c) 1.00 wt.% carbon black.

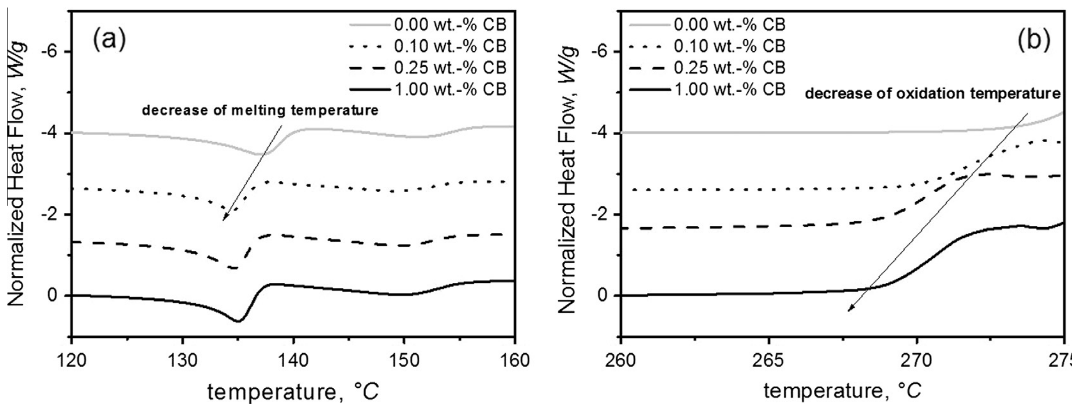

Fig. 2. DSC thermograms of PP-RCT CB-MB compounds in (a) the melting and (b) the oxidation regime in the 2nd heating interval. The grey curve represents the thermogram of the unpigmented reference compound.

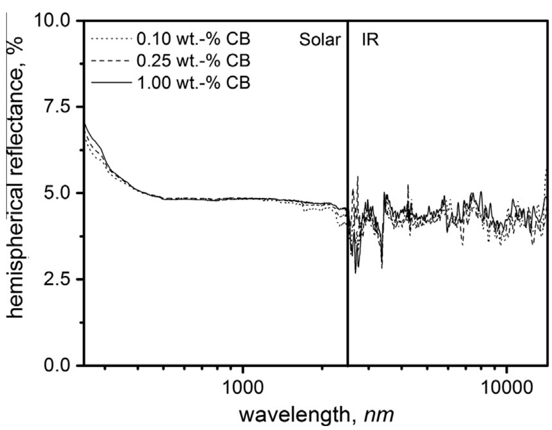

Fig. 3. Hemispherical solar and infrared reflectance spectra for 2 mm thick black pigmented PP-RCT plaques.

As depicted in Fig. 4 the hemispherical transmittance in the solar wavelength range is negligible. In the infrared region a slight hemispherical transmittance was obtained, which was more pronounced for compounds with low carbon black contents (0.10 and 0.25 wt.%) at 4500 to 6000 nm and above 12000 nm. The integral infrared transmittance values weighted with black body functions at 100 °C were ranging from 1.0% for highest pigment concentration to 2.0% for lowest carbon black concentration (see Table 1). For the integral infrared emittance values ranging from 93.7% to 94.7% were obtained with the lower value only for the grade with 0.10 wt.%.

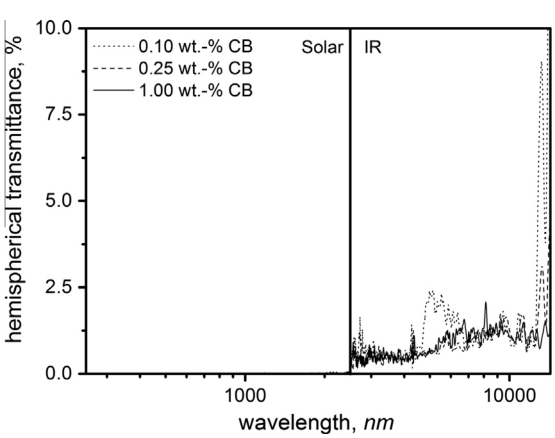

Fig. 4. Hemispherical solar and infrared transmittance spectra for 2 mm thick black pigmented PP-RCT plaques.

3.3. Mechanical properties

In Fig. 5 representative stress–strain curves from tensile tests are shown for unpigmented and carbon black pigmented PP-RCT specimens. The shape of the stress–strain diagrams was comparable exhibiting a yield point at about 10% strain, a necking of samples and a plastic deformation regime with strain hardening at strain values of about 300%. Characteristic mechanical properties for the specimen with varying carbon black loading are summarized in Table 2. The unpigmented reference material exhibited a Young's modulus of 1040 MPa, a yield stress of 26.5 MPa and a strain-at-break of 465%. Regarding the modulus slightly lower values were obtained only for specimen with carbon black masterbatch content of 0.75 and 1.00 wt.%. For these specimens also the yield stress values were slightly lower. With exception of the specimen with 0.10 wt.% carbon black masterbatch also the strain-at-break values were almost comparable and within the scattering limits.

3.4. Aging behaviour

In Fig. 6 representative DSC thermograms of the first heating run in the unaged state and after exposure intervals of 168, 2016 and 3024 h in 135 °C hot air are depicted for 1.00 wt.% carbon black masterbatch compounds. As mentioned above, PP-RCT crystallizes in α- and β-form so that two melting peaks are detectable. Kahlen et al. (2010a, 2010b) described a significant increase in the degree of crystallinity after short intervals of exposure, related to post- and/or re-crystallization. Moreover β-to-α recrystallization and a pronounced shift in melting peak temperature in hot

Table 1
Characteristic integral solar- and infrared-optical properties of the black-pigmented PP-RCT specimen. The integral infrared optical values have been calculated by weighting with black body functions at 100 °C.

Compound	Solar absorbance (%)	Infrared reflectance (%)	Infrared transmittance (%)	Infrared emittance (%)
PP-RCT/0.10 wt.% CB	95.2 ± 0.1	4.3 ± 0.1	2.0 ± 0.1	93.7 ± 0.1
PP-RCT/0.25 wt.% CB	95.1 ± 0.1	4.2 ± 0.2	1.2 ± 0.1	94.6 ± 0.2
PP-RCT/0.50 wt.% CB	95.2 ± 0.1	4.2 ± 0.1	1.1 ± 0.0	94.7 ± 0.1
PP-RCT/0.75 wt.% CB	95.1 ± 0.1	4.4 ± 0.0	1.0 ± 0.2	94.6 ± 0.1
PP-RCT/1.00 wt.% CB	95.2 ± 0.1	4.4 ± 0.1	1.0 ± 0.2	94.6 ± 0.2

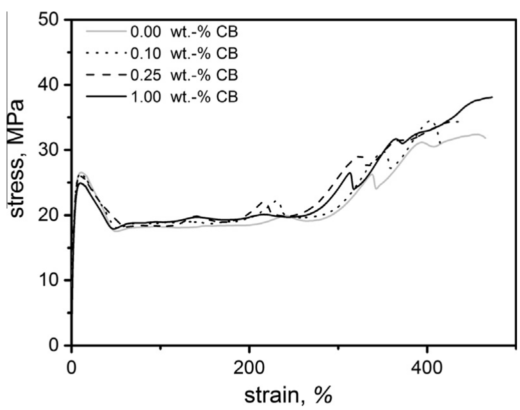

Fig. 5. Stress–strain curves of the investigated 5A specimen with varying carbon black pigmentation.

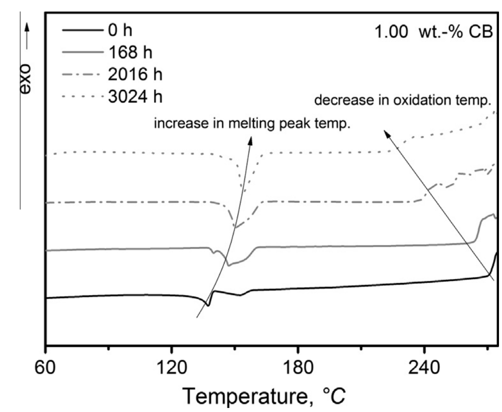

Fig. 6. DSC thermograms of pigmented PP-RCT films (1.00 wt.% CB) exposed to 135 °C hot air for 0, 168, 2016 and 3024 h.

air take place after short time of exposure. These physical changes are in good agreement with findings described by Kotek et al. (2004), Šćudla et al. (2003) and Groff et al. (1996) for various unpigmented PP grades.

In the oxidation temperature regime a significant reduction of T_{ox} was obtained for all investigated compounds. The shift in oxidation temperature is dependent on exposure time. The upper part of Fig. 7 depicts that higher amounts of carbon black lead to a more pronounced decrease of the oxidation temperature. PP-RCT pigmented with 1.00 wt.% of carbon black revealed oxidation temperatures of 230 °C after already 2000 h, whereas the oxidation temperature of compounds with lower concentrations like 0.10 and 0.25 wt.% carbon black fell below 230 °C after approximately 3000 h of exposure in hot air at 135 °C.

The better long-term stability of PP-RCT with low carbon black contents is also reflected by ultimate strain values obtained by tensile testing. As depicted in Fig. 7, first a significant decrease of the strain-at-break values within

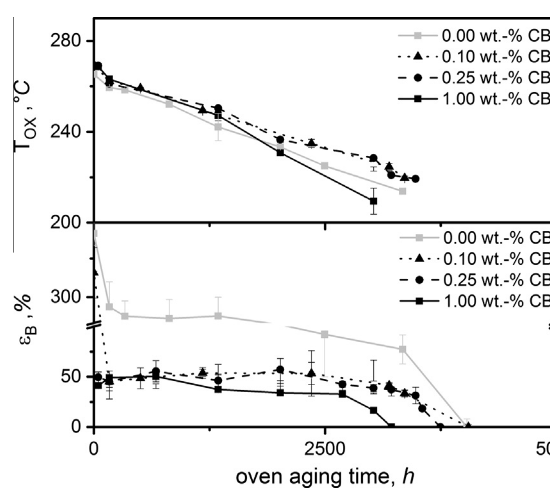

Fig. 7. Oxidation temperature (T_{ox}) and strain-at-break (ε_B) for unpigmented and pigmented PP-RCT films versus oven aging time in hot air at 135 °C.

Table 2
Characteristic mechanical properties of the black pigmented PP-RCT specimen.

Compound	Young's modulus (MPa)	Yield stress (MPa)	Strain-at-break (%)
PP-RCT/0.00 wt.% CB	1040 ± 20	26.5 ± 0.3	465 ± 7
PP-RCT/0.10 wt.% CB	1020 ± 35	26.0 ± 0.5	419 ± 7
PP-RCT/0.25 wt.% CB	992 ± 42	26.1 ± 0.2	437 ± 11
PP-RCT/0.50 wt.% CB	1030 ± 56	26.3 ± 0.3	436 ± 22
PP-RCT/0.75 wt.% CB	934 ± 19	24.9 ± 0.3	474 ± 43
PP-RCT/1.00 wt.% CB	870 ± 55	24.9 ± 0.5	472 ± 42

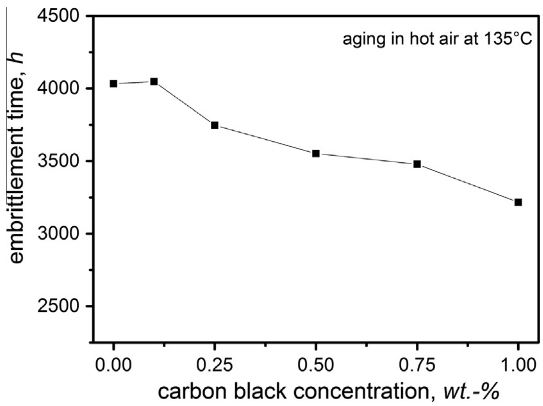

Fig. 8. Maximum embrittlement time (in hours) versus carbon black concentration for thermo-oxidative degradation in hot air at 135 °C.

48 h, related to post-crystallization can be observed. Subsequently, the strain-at-break values remained constant for exposure times up to 2500 h. In this induction time period slow oxygen uptake associated with stabilizer consumption takes place (Schwarzenbach et al., 2009). Following the induction period, embrittlement was observable. The time-to-embrittlement is significantly dependent on the concentration of carbon black pigments. While the embrittlement time for PP-RCT with 1.00 wt.% carbon black was about 3200 h, the unpigmented PP-RCT and the grade with 0.10 wt.% carbon black exhibited embrittlement time of about 4000 h. In Fig. 8 the embrittlement time of the various grades is plotted as a function of pigment concentration. The relationship clearly indicated, that the content of the investigated carbon black type should be 0.1 wt.% or less.

4. Summary and conclusions

Black solar absorber compounds based on polypropylene (PP) with varying concentrations of carbon black were prepared using a twin-screw extruder. Specimens were characterized as to the morphological, thermo-analytical, solar and infrared optical, mechanical properties and the aging behaviour in hot air. In comparison to previous investigations a quite homogeneous dispersion of the carbon black masterbatch in the polypropylene matrix was achieved for all concentrations. Microscopical observations revealed small spherical carbon black domains with diameters smaller than 0.5 μm. Slightly independent on pigment concentration high solar absorbance values of about 95% were achieved. The solar transmittance of the 2 mm thick specimen was negligible. In the infrared range a low transmittance was observable for grades with carbon black contents. Also the mechanical properties of the PP-grades with different carbon black loadings were only slightly affected. The incorporation of carbon black pigments resulted in a decrease of the Young's modulus and the yield stress by 15% and 6%, respectively. The basic investigations proved that the investigated PP grades are of high potential for black absorbers of collectors with overheating control. Regarding the long-term behaviour preliminary exposure test in hot air at 135 °C were carried out using micro-sized specimen. Aged specimens were characterized as to changes of to the oxidation temperature and the strain-at-break. Depending on the carbon black content significant differences in the reduction of oxidation temperatures and strain-at-break values was obtained. Hence, it can be concluded that compounds with low carbon black concentrations are the most promising candidates for glazed solar thermal collectors, in which the glazing provides a UV protection of the polymeric solar absorber.

Acknowledgments

This research work was performed in WP-04 of the cooperative research project *SolPol-2* entitled "Solar-thermal systems based on polymeric materials" (www.solpol.at). This project is funded by the Austrian Climate and Energy Fund (KLI:EN) within the programme "Neue Energien 2020" and administrated by the FFG. The authors wish to express their acknowledgements to S. Kahlen, K. Stubenrauch and A. Meinecke (Borealis, Linz, A) for the cooperation, especially for making available the compounds.

References

Allen, N.S., Edge, M., Corrales, T., Childs, A., Liauw, C.M., Catalina, F., 1998. Ageing and stabilisation of filled polymers: an overview. Polym. Degrad. Stab. 61 (2), 183–199.

Bernreiter, K., Wolfschwenger, J., 2002. Method for increasing the ratio of beta-modification in polypropylene. Patent EP 0682066B2.

Bird, R.E., Hulstrom, R.L., Lewis, L.J., 1983. Terrestrial solar spectral data sets. Sol. Energy 30 (6), 563–573.

Buxbaum, G., 1998. Industrial Inorganic Pigments, second ed. Wiley-VCH.

Groff, I., Franzese, R., Landro, L.D., Pagano, M.R., Genoni, M., 1996. Characterization of polypropylene pipes during accelerated aging in air and water. Polym. Test. 15, 347–361.

Horrocks, A.R., Mwila, J., Miraftab, M., Liu, M., Chohan, S.S., 1999. The influence of carbon black on properties of orientated polypropylene – 2. Thermal and photodegradation. Polym. Degrad. Stab. 65 (1), 25–36.

Jakab, E., Blazsó, M., 2002. The effect of carbon black on the thermal decomposition of vinyl polymers. J. Anal. Appl. Pyrol. 64 (2), 263–277.

Jakab, E., Omastová, M., 2005. Thermal decomposition of polyolefin/carbon black composites. Pyrolysis 74 (1-2), 204–214.

Kahlen, S., Wallner, G.M., Lang, R.W., 2010a. Aging behavior of polymeric solar absorber materials – Part 2: commodity plastics. Sol. Energy 84 (9), 1577–1586.

Kahlen, S., Jerabek, M., Wallner, G.M., Lang, R.W., 2010b. Characterization of physical and chemical aging of polymeric solar materials by mechanical testing. Polym. Testing 29 (1), 72–81.

Kotek, J., Kelnar, I., Baldrian, J., Raab, M., 2004. Structural transformations of isotactic polypropylene induced by heating and UV light. Eur. Polym. J. 40, 2731–2738.

Kurzböck, M., Wallner, G.M., Lang, R.W., 2012. Black pigmented polypropylene materials for solar absorbers. Energy Procedia 30, 438–445.

Levinson, R., Berdahl, P., Akbari, H., 2005. Solar spectral optical properties of pigments – Part II: survey of common colorants. Sol. Energy Mater. Sol. Cells 89 (4), 351–389.

Mayer, R., 1991. The Artist's Handbook of Materials and Techniques, fifth ed. Viking Penguin.

Meir, M., Ochs, F., Wilhelms, C., Wallner, G., 2012. State of the Art: Polymeric Materials in Solar Thermal Applications. Polymeric Materials for Solar Thermal Applications. Wiley-VCH, pp. 219–242.

Schwarzenbach, K., Gilg, B., Müller, D., Knoblauch, G., Pauquet, J.-R., Rota-Graziosi, P., Schmitter, A., Zingg, J., 2009. Antioxidants. In: Zweifel, H., Maier, R.D., Schiller, M. (Eds.), Plastics Additives Handbook, sixth ed. Hanser, Munich, pp. 1–137.

Ščudla, J., Raab, M., Eichhorn, K.-J., Strachota, A., 2003. Formation and transformation of hierarchical structure of β-nucleated polypropylene characterized by X-ray diffraction, differential scanning calorimetry and scanning electron microscopy. Polymer 44, 4655–4664.

Wallner, G.M., Lang, R.W., 2005. Guest editorial. Polym. Mater. Solar Energy Appl. 79 (6), 571–572.

Wallner, G.M., Grabmayer, K., Beissmann, S., Schobermayr, H., Buchberger, W., Lang, R.W., 2013. Methoden zur beschleunigten Alterungsprüfung von Kunststoffen. Erneuerbare Energien 2013–1, 18–20.