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Energy Procedia 30 (2012) 438 – 445
Energy Procedia

SHC 2012

Black pigmented polypropylene materials for solar absorbers

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Abstract

Polyolefin materials are of high relevance and interest for absorbers of solar thermal collectors with integrated overheating protection. In this work the effect of various black pigments (carbon black (CB) and carbon nanotubes (CNT)) on optical and mechanical properties of PP-RCT grades (Polypropylene-Random Copolymer with special crystalline structure (ß phase) for elevated temperature applications) is investigated. To meet the requirements of high absorbance in the solar wavelength range (> 90%) and enhanced mechanical properties at service temperatures up to 90°C for at least 10 years, black pigmented specimens are characterized in an unaged state by UV/Vis/NIR-spectrometry and tensile testing. The experimental results reveal small nanoscalic carbon black pigments as suitable candidates for the pigmentation and improved absorbance behavior of overheating protected polymeric solar thermal absorbers. The investigated black compounds exhibit integral solar absorbance values between 95 and 96 %. The mechanical properties are significantly affected by the distribution quality of the black pigments. In current research special attention is given to the aging behavior of the developed compounds for solar absorbers.

Keywords: Solar thermal; absorber; polypropylene; carbon black; carbon nanotube

1. Introduction

In the end of the year 2010 the total area of installed solar collectors equaled 279.7 million square meters corresponding to a solar heating capacity of approximately 195.8 GWth [1].While the scarcity of absorber materials like copper is an increasing problem of the solar thermal industry, an all-polymeric solar absorber has the benefit of sufficient availability and costs. Plastics are material grades with a worldwide production volume of 265 million tons per year (2011) and a dynamically growth rate among

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doi:10.1016/j.egypro.2012.11.052

various end use segments [2]. Currently commodity plastics such as polyethylene (PE) and polypropylene (PP) are mainly used for swimming pool absorbers, nevertheless they offer high potential in glazed collectors with appropriate overheating protection (integrated storage collectors or vented flat-plate collectors (e.g. Type: eco-FLARE; Magen Eco Energy)). PP is rather sensitive to carbon black pigmentation [3-5]. While for already used PP grades like PP-H (Polypropylene-Homopolymer) and PP-B (Polypropylene Block-Copolymer) no certifications for pressurized pipes are existing, PP-RCT (Polypropylene-Random Copolymer with special crystalline structure (ß phase) for elevated temperature applications) is an interesting candidate for pressurized black solar thermal absorbers due to its superior hydrostatic pressure performance and improved resistance against high stress levels, resulting from induced stable hexagonal β phase lamellae, with coplanar stacks [6, 7].

Since only unpigmented PP-RCT compounds have been investigated so far, main emphasis of this study carried out in the multilateral research project SolPol-2 (www.solpol.at) is the development of black pigmented PP-RCT compounds and the investigation of short-term properties [8-11]. To fulfill the requirements of high absorbance in the solar wavelength range of more than 90 % compounds of PP-RCT and carbon blacks, as well as carbon nanotubes with different properties are formulated. To meet service temperatures of 90 °C for at least 10 years and to investigated long-term properties further research will be presented in another part of a publication series.

2. Experimental

2.1. Materials

Commercially available polypropylene random copolymer (PP-RCT) was supplied by Borealis AG, Austria. The grade has a melt flow rate of 0.3 g/10 min (230 °C/2.16 kg). Table 1 offers detailed information as to the four compounded pigmented PP-RCT grades and the unpigmented reference grade. The selected matrix polymer grade PP-RCT offers higher β-phase content and a proper stabilisation for elevated temperature applications. According to information of the material supplier the PP-RCT grade contains an increased content of phenolic and phosphitic antioxidants, however, no detailed information about the used stabiliser system and content is available. The experimental design involves parameters of the investigated pigments including particle size and morphological structure (Tables 1 & 2).

Table 1. Investigated unpigmented (reference) and pigmented polypropylene-random copolymer compounds (PP-RCT) (polymer nomenclature; polymer concentration; nucleation; black pigment type; pigment size)

Polymer	Concentration [wt.-%]	Nucleation	Black Pigments	Pigment Size [nm]
PP-RCT	100.00	Beta-nucleated	-	
PP-RCT	98.50	Beta-nucleated	Carbon Black 1 (CB1)	14
PP-RCT	98.50	Beta-nucleated	Carbon Black 2 (CB2)	20
PP-RCT	98.50	Beta-nucleated	Carbon Black 3 (CB3)	56
PP-RCT	98.50	Beta-nucleated	Carbon Nanotubes (CNT1)	100 - 200

Table 2. Investigated pigment types (pigment nomenclature; blackness value M_Y; BET surface area)

Pigment	Blackness Value M_Y	BET Surface Area [m^2/g]
Carbon black (CB1)	265	300
Carbon black (CB2)	245	120
Carbon black (CB3)	230	45
Carbon nanotubes (CNT1)		17-25

A two-step mixing process was used to get homogeneously dispersed black-pigmented PP-RCT. First before blending, masterbatches with CB and CNT pigments were prepared. Afterwards the resulting composites were obtained by extruding fresh PP granules sidefeeded with the related pigment masterbatch in a twin-screw extruder (Type: Prism TSE 24 HC; Thermo Fisher Scientific Inc.; Waltham, MA, USA) at TCKT Wels (Transfercenter für Kunststofftechnik GmbH; Wels; Austria). Therefore the used masterbatches were simultaneously gravimetric metered in the correct blend ratios by material hoppers. To provide best blend homogeneity the masterbatch flow was controlled through a cascade chamber where they were extruded at a screw speed of 400 rpm. After pelletizing, the pigmented PP-RCT grades were compression-moulded into 2 mm thick plates. The final composites contain ~ 1.5 wt. % of diverse carbon black pigments and carbon nanotubes. To obtain a reference specimen with the same thermo-mechanical history, neat PP-RCT was similarly processed. Tensile test specimens of the 5A type (ISO 527-2/5A) with an overall length of 75 mm were machined with a puncher.

2.2. Methodology

For the evaluation of the influence factors of investigated pigments on solar optical and mechanical properties, UV/Vis/NIR spectrometry and tensile testing was applied. To detect the influence of pigmentation on the morphology of the β-nucleated PP-RCT grades, wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) were used. Optical light microscopy in transmitted light mode, was applied to prove the dispersion of the carbon black pigments.

The normal-hemispherical transmittance τ_{nh} and reflectance ρ_{nh} values for the compounded black PP-RCT specimens were obtained using a Perkin Elmer Lambda 950 Ulbricht sphere spectrophotometer (Perkin Elmer GmbH; Rodgau; Germany). The Ulbricht sphere of the spectrometer had a diameter of 150 mm and the values were measured at normal-hemispherical transmittance measurement, and normal-hemispherical reflectance measurement. For the calculation of the solar hemispherical absorbance of black pigmented PP-RCT compounds integral hemispherical reflectance and transmittance values over the solar wavelength range, as input parameters were required. First normal-hemispherical transmittance and reflectance values of 50 x 50 x 2 mm^3 plaques were measured. Afterwards the spectral data were averaged by weighting the measured spectral data in steps of 5 nm by the AM 1.5 global solar irradiance source function, given in Bird and Hulstrom, 1983 [12]. Finally the integral hemispherical absorbance value for each plaque was calculated, based on the weighted integral transmittance and reflectance values.

Thermal analysis was carried out using a Perkin Elmer DSC 4000 (Perkin Elmer GmbH; Rodgau; Germany). The difference amount of heat to increase the temperature of a sample (polymer compound sealed in an aluminum pan) in comparison to a reference sample as a function of temperature is measured to determine thermal properties of specimens, like glass transition (endothermic), crystallisation and oxidation (exothermic). For this thermo-analytical method specimens with a mass range of 5-10 mg were placed in 30 µl aluminium pans and closed with perforated lids. Thermographs were recorded in heating/cooling/heating cycles with heating/cooling rates of 10 K min^{-1} under static air purge. According to Patent EP 0682066B2 for the β phase content determination the 2nd heat-up ramp has to be considered, to ensure the elimination of thermal and mechanical process memory of the samples. Therefore all shown diagrams refer to the 2nd heating scan and include deducible characteristic values of at least 5 testings. β phase content of the investigated PP-RCT grades was calculated by correlation of the peak areas. The results of the method were supported and correlated with wide angle X-ray scattering measurements at the laboratories of Borealis AG, Linz.

A series of tensile tests was carried out according to DIN EN ISO 527-2 (1996) using a screw driven universal testing machine (Type: Zwick Line Z5.0; Zwick GmbH & Co. KG; Ulm, Germany). The tests were performed with an initial clamping length of 50 mm and a test speed of 50 mm/min. All 5A specimens were tested in an unaged state to obtain information about mechanical properties and deformation mechanisms. From a total number of at least 5 specimens for each test series average values for Young's modulus, E_T, tensile strength, σ_M, and strain at break, ε_B were deduced. The displacement values were determined using a multi-extensometer.

For the determination of the pigment dispersion and further investigation and correlations of mechanical properties and the morphology of the PP-RCT grades an optical microscope (Type: BX 61; Olympus Austria GmbH; Vienna, Austria) with 5x, 50x and 100x objectives was used in reflective mode. The precise motorised focus of the microscope drive offers the possibility of 3D imaging in high resolution by Extended Focal Imaging (EFI).

3. Results and discussion

3.1. Solar optical properties

Since the normal-hemispherical transmittance values of all black pigmented PP-RCT plaques with thickness of 2 mm were negligible, only the normal-hemispherical reflectance spectra, relevant for the solar absorbance, are described and discussed (Fig. 1). To illustrate the deducible differences according optical properties for different black pigmentation the spectra are shown in Fig. 1.

The artefacts, in the spectra can be attributed to a detector change at 860 nm and a higher detector noise in the near infrared wavelength region (above 860 nm). The carbon nanotube pigmented specimen PP-RCT/CNT1 showed the lowest reflectance values of all investigated grades over the solar wavelength range. The spectral differences of the various carbon black pigmented grades are low. In Table 3 the integral solar absorbance values are depicted along with information to the black pigments. For the carbon black pigmented PP-RCT grades, a correlation of the blackness value M_Y and relative tinting strength with the solar is deducible.

Table 3. Solar optical absorbance values of black-pigmented PP-RCT grades in correlation with pigment properties.

Compound	Pigment Size [nm]	Solar absorbance [%]	Blackness value M_Y	Relative tinting strength
PP-RCT	-	31.9	-	
PP-RCT/CB1	14	95.5	265	124
PP-RCT/CB2	20	95.3	245	109
PP-RCT/CB3	56	95.2	230	95
PP-RCT/CNT1	100 - 200	95.9		

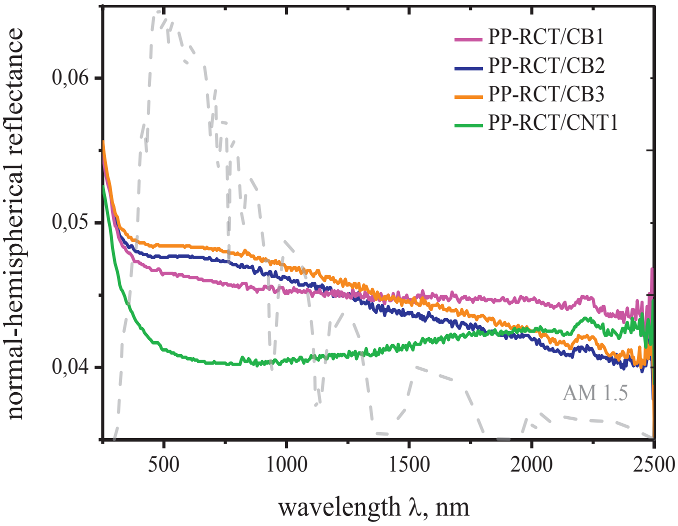

Fig. 1. Normal-hemispherical solar reflectance spectra for 2 mm thick black pigmented PP-RCT plaques; the grey curve represents the AM 1.5 spectrum used to calculate non-spectral integral values.

3.2. Thermo-analytical characteristics

In Fig. 2 characteristic DSC thermograms of the second heating run are shown. The unpigmented reference sample PP-RCT exhibits a double melting peak, which is common for beta-nucleated polypropylene. The melting peak temperatures for the hexagonal β-crystallites and the monoclinic α-crystallites are at 137 °C and 151 °C, respectively. The oxidation temperature of the reference specimen was at 273 °C, the crystallization temperature at 111 °C. The melting and recrystallization transition of β-nucleated random-copolymer polypropylene are about 10 °C lower than for isotactic PP. This can be attributed to the more irregular structure of the chain [13].

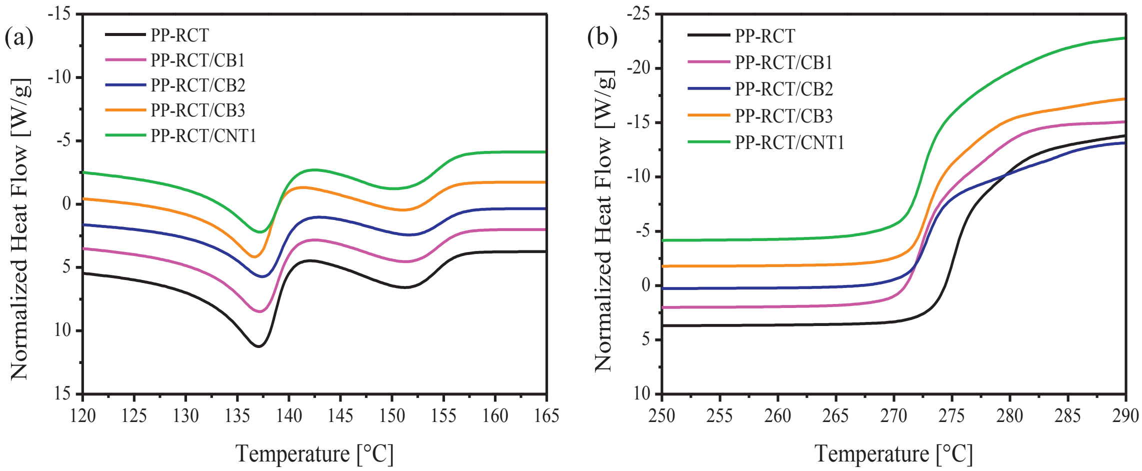

Fig. 2. DSC thermograms of PP-RCT/CB and CNT nanocomposites during (a) melting and (b) oxidation processes in the 2nd heating interval. The black curve reveals thermal properties of the unpigmented reference compound.

To determine the β phase content of the specimens the peak areas of the melting peaks are correlated. For the unpigmented reference material a β-phase content of 79 and 81 % were determined by DSC and WAXS, respectively. Concerning the pigmented PP-RCT grades, the incorporation of carbon nanotubes into the polypropylene random-copolymer matrix leads to a decrease of the β phase content. In contrast, the carbon black pigmentation did not affect characteristic temperatures or β phase content. The oxidation temperature of the pigmented compounds slightly decreased from 273°C to 271°C.

3.3. Mechanical properties

Results of tensile testing measurements are shown in Table 4. The unpigmented reference material exhibits highest Young's modulus and strain-at-break values. As to the pigmented specimens slightly higher tensile strength and lower strain at-break values were obtained for the grades with carbon black. This is in good agreement with results described in the literature for 1.5 wt.-% modified grades [10]. The carbon nanotube pigmented compounds reveal a significant decrease in the mechanical properties tensile strength and strain at break. This is in contrast to data provided in the literature provided by Song et al. [14]. Nanocomposites are significantly dependent on the dispersion of the pigment [8-10]. To obtain explanations on the controversial results of carbon nanotubes pigmented PP-RCT compounds microscopic investigations were undertaken. Moreover, since the concentration of the pigment in the compound indicates the highest effect on the mechanical properties further investigations will be presented in part II of the publication series.

Table 4. Characteristic mechanical properties of the PP-RCT in correlation with the chemical structure of the investigated pigments.

Compound	Young's Modulus [MPa]	Tensile Strength [MPa]	Strain-at-break [%]	Pigment BET Surface Area [m^2/g]
PP-RCT	1040 ± 20	32.3 ± 0.8	465 ± 7	
PP-RCT/CB1	915 ± 15	33.3 ± 1.8	414 ± 20	300
PP-RCT/CB2	910 ± 18	34.5 ± 0.8	417 ± 10	120
PP-RCT/CB3	931 ± 21	35.6 ± 1.8	438 ± 16	45
PP-RCT/CNT1	958 ± 33	30.1 ± 4.8	377 ± 54	17-25

3.4. Morphology

Optical micrograph images of 50 µm thin slices of the compression moulded compound PP-RCT/CB2 and PP-RCT/CNT1 are displayed in Fig. 3. For the carbon black modified grade a good dispersion is observable (Fig. 3a). Small agglomerates with a diameter of about 0.5 µm are dominating. In contrast, the compound with carbon nanotubes exhibits an irregular distribution of the incorporated particles with agglomerates of different size. The size of the domains with carbon nanotubes is ranging from 0.5 to 60 µm. The lower mechanical properties of the PP-RCT/CNT compound can be attributed to the inhomogeneous distribution of the CNT pigment.

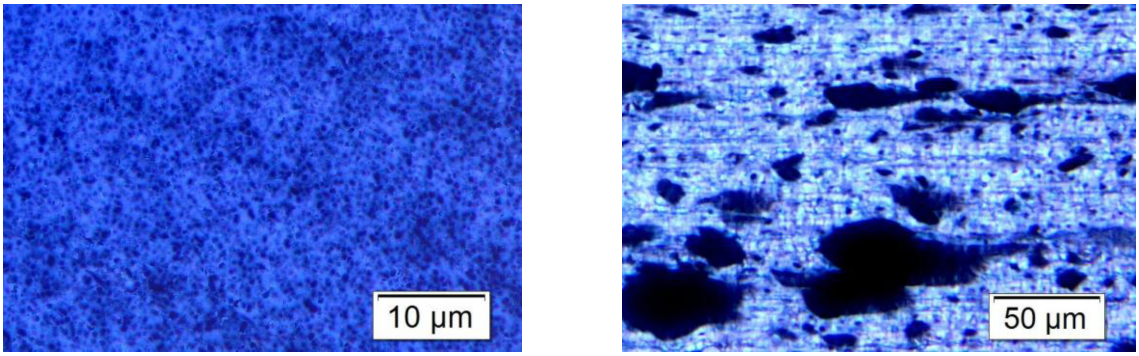

Fig. 3. Micrographs of (a) PP-RCT/CB1 nanocomposites and (b) and PP-RCT/CNT1 nanocomposites. The black domains represent the pigment agglomerations, while the PP-RCT matrix is coloured blue.

4. Conclusions

For black solar absorbers compounds of polypropylene (PP) and 1.5 wt.-% black pigments (carbon nanotubes and carbon black) were prepared using a twin-screw extruder. Two mm thick plaques were characterized as to the optical, thermo-analytical, mechanical and morphological properties and structures. The solar absorbance was nearly independent of pigment type ranging from 94 to 95%. In contrast, the mechanical properties were significantly affected by the pigment type. While carbon black had a small effect on the ultimate mechanical properties (slight increase in tensile strength and decrease in strain-at-break), the compound with carbon nanotube pigments showed significantly lower ultimate mechanical properties. The differences in the mechanical properties could be attributed to the more irregular distribution of carbon nanotube pigments with agglomerates in the µm range. Carbon nanotubes also influence the crystal phase formation resulting in lower values of ß-crystallinity, which is of importance for the long-term performance.

The basic investigations revealed that the investigated PP grades are of high potential for black absorbers of collectors with overheating control. In ongoing investigations special attention is given to the long-term behavior under application-relevant loading conditions.

Acknowledgements

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". The authors wish to express their acknowledgements to K. Klimke, S. Kahlen and A. Meinecke (Borealis, Linz, A) for the cooperation, especially for making available the compounds.

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