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Absorber materials based on polymer nanocomposites containing silver nanoparticles for solar thermal collectors

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ABSTRACT

This study describes the synthesis and characterization of polymer-based nanocomposites to fabricate absorber materials for solar thermal collectors. Heat generation by nanosized silver particles (NSP) under irradiation with light of appropriate wavelength is exploited for an efficient harvesting of solar energy. NSP were synthesized by reduction of silver nitrate ($AgNO_3$) in a methacrylate resin. The photothermal conversion of solar energy into heat is optimized by increasing the overlap between the plasmonic band of the NSP and the spectral emission of the sun. Thus, the synthesis conditions were adjusted in order to broaden the plasmon absorption band of the resultant NSP. The UV–vis spectra of suspensions containing 300 ppm NSP exhibited a broad absorption band in the range between 360 and 1100 nm with three absorption peaks at 335, 440, and 700 nm. These absorption bands are associated to the presence of triangular NSP, which was confirmed by TEM microscopy. The resins containing NSP were activated with benzoyl peroxide and polymerized after 20 min at 80 °C. The photothermal conversion effect of the nanocomposites was assessed by monitoring the temperature increase with fine thermocouples embedded in 2-mm thick specimens during irradiation with light of different wavelength. The temperature reached during irradiation of nanocomposites showing a very broad absorption band was 115 °C while that of the nanocomposites exhibiting a single peak was 102 °C.

1. Introduction

The rising cost of fossil fuels and a growing level of environmental awareness over the past two decades have encouraged the use of solar energy in thermal applications. Solar thermal collectors are devices that convert electromagnetic solar radiation energy into heat (Tian and Zhao, 2013; Thirugnanasambandam et al., 2010; O'Hegarty et al., 2016). In general, solar collectors are classified into three categories according to the operating temperature, high temperature ($\geq$1000 °C), intermediate temperature ($\sim$300 °C) and low temperature ($\leq$100 °C). The most common type of low-temperature solar collectors consists of a blackened plate to absorb solar radiation and tubes containing a heat-transport fluid to remove heat from the absorber (Tian and Zhao, 2013; Thirugnanasambandam et al., 2010; O'Hegarty et al., 2016). The absorber plate is covered by a highly transmissive glass cover to allow the maximum amount of solar energy to be incident on its surface while minimizing heat losses. In addition, the plate is surrounded by insulation in order to reduce heat losses (Beikircher et al., 2015). Conventional absorber plates are fabricated from metals coated with paints, which absorb solar energy more efficiently than common black paint (Mason,1983). Alternatively, direct absorption solar collectors are a new type of solar collectors that use a suspension of nanoparticles (NNP) in a conventional base fluid (nanofluid). In these thermal collectors the solar radiation is absorbed by the suspension of NNP, which acts as both absorber and heat transfer medium (Sarsam et al., 2015). Studies on the photothermal conversion of nanofluids prepared from silver (Yu and Xuan, 2018), gold (Jeon et al., 2016; Wang et al., 2017a,b) and graphene (Fan et al., 2017) have been recently reported. Although the use of nanofluids in solar collectors has showed a good performance, there are still some issues such as the high cost of producing nanofluids as well as instability and agglomeration of the NNP that need to be addressed (Qin et al., 2017; Holm et al., 2017; Sharaf et al., 2018).

Currently, the fundamental principles that govern the performance of flat-plate collectors are well understood and significant research effort has been focussed on the development of novel materials for high-performance solar thermal collectors (Granqvist and Niklasson, 2018; Khan et al., 2018). The most important component of solar collectors is the absorber surface as it determines the speed and efficiency of photothermal conversion of solar energy into heat. Polymeric materials

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present the advantage of both weight and cost reduction, which make them very attractive candidates for solar thermal collectors. Recent studies have described absorber materials prepared from biopolymers (Klein et al., 2017), and films of a polymer with embedded gold (Shang et al., 2017) and silver (Mishra et al., 2010; Barrera et al., 2018) NNP.

It is well known that noble metal NNP liberate heat when exposed to light. Photoexcitation of the conduction electrons of the NNP induces surface plasmon oscillations, which liberate heat as a result of non-radiative relaxation pathways (Baffou and Quidant, 2013). Although heat liberation in noble metal NNP was considered a secondary effect, over the last decade, it has been demonstrated that noble metal NNP can serve as efficient nanosources of heat giving rise to a new set of applications of technological interest such as photothermal therapy to treat cancer (Aberasturi et al., 2015) and steam generation (Wang et al., 2017a,b).

The objective of this study was the synthesis of polymeric absorber materials to be used in low-temperature solar collectors (≤100 °C) which consist of a plate to absorb solar radiation and tubes containing a heat-transport fluid to remove heat from the absorber. Suspensions of NSP were prepared in methacrylate monomers using acrylonitrile as stabilizer. Experimental conditions were adjusted in order to achieve a broad plasmonic band of the resultant NSP. The resins containing NSP were polymerized and the photothermal conversion effect of the resulting nanocomposites was examined.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, ≥99%, Sigma Aldrich, USA). Benzoyl peroxide (BPO, ≥97%, Sigma Aldrich, USA), 2,6-di-tert-butyl-p-cresol (BHT, ≥99%, Sigma Aldrich, USA) and acrylonitrile (ACN, 99%, Sigma Aldrich, USA) were employed as received. The methacrylate resins 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]-propane (BisGMA, 90%) and 2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane (MetB, 98%) were from Esstech, USA. Triethylene glycol dimethacrylate (TEGDMA, 95%) was from Aldrich, USA. MetA represents a mixture (70/30) BisGMA/TEGDMA weight ratio. The manufacturers add different inhibitors to the methacylate resins to prevent polymerization during storage (Asmussen and Vallo, 2015). In addition, we added 200 ppm 2,6-di-tert-butyl-p-cresol (BHT) inhibitor to the resins. As reported by the manufacturers the viscosity of MetA is 5.7 Pa·s while that of ACN is $3.4 \cdot 10^{-4}$ Pa·s. The structure of the reactants is shown in Fig. 1. Irradiation of the nanocomposites was carried out with light emitting diodes (LEDs) with its irradiance centred at 410, 465, 520 and 630 nm (D + LED, Argentina). Specimens used in photothermal conversion studies were irradiated by the LED placed at 5 mm from the specimen surface. The power emitted by the LEDs at a distance of 5 mm was set equal to 50 mW. In addition, a white 7 W LED (Osram, BO-F7OSKD) was used.

2.2. Preparation of NSP

$AgNO_3$ was first dissolved in ACN at silver mass fraction equal to 3 wt% (solution M). Suspensions of NSP were prepared from blends of 1 g of solution M and the appropriate amount of MetA. NSP were synthesized in MetA by reduction of $AgNO_3$ by the polymerization inhibitors present in the resin (Asmussen and Vallo, 2015). Specimens for photothermal conversion studies were also prepared from suspensions of spherical NSP in MetB resin. Details of the synthesis of spherical NSP were reported elsewhere (Asmussen and Vallo, 2015). Photothermal conversion in nanocomposites derived from these suspensions were used in this study for comparative purposes.

2.3. Characterization studies

UV–vis absorption spectra were acquired with a 1601 PC Shimadzu spectrophotometer. Sample preparation was described elsewhere (Asmussen and Vallo, 2015). The formation of NSP at temperatures higher than room temperature was monitored using a temperature-controlled sample holder accessory of the UV–visible spectrophotometer.

The morphology of the NSP was examined by electron microscopy (Philips CM-12 transmission electron microscope). Samples were prepared as described elsewhere (Asmussen and Vallo, 2015).

2.4. Polymerization of resins containing NSP

Polymerization of suspensions of NSP in MetA was monitored by Fourier transform infrared in the near range (NIR) using a Nicolet 6700 Thermo Scientific spectrophotometer. Polymerization of resins containing NSP and activated with 1 wt% BPO, was carried out at 80 ± 2 °C. The degree of conversion was assessed by monitoring the band assigned to the methacrylate functional group (6165 cm^{-1} in the NIR).

2.5. Temperature measurements

Photothermal conversion effects were examined by monitoring temperature changes during irradiation of nanocomposite materials with the light sources described in item 2.1. The temperature was monitored with fine thermocouples (K-type, Omega Engineering Inc., USA, precision ± 0.5 °C) inserted in 2 mm thick specimens. The diameter of the specimens was either 10 or 20 mm. The thermocouple was placed carefully in the middle of the thickness and then the assembly was placed in the oven at 80 °C to polymerize the resins.

3. Results and discussion

3.1. Preparation and characterization of NSP

NSP were synthesized by reduction of $AgNO_3$ in MetA methacrylate resin. The reducing agents of the silver ions were the inhibitors added to the resin to avoid premature polymerization (Asmussen and Vallo, 2015). $AgNO_3$ is not soluble in the methacrylate resin; therefore it was first dissolved in a small amount of ACN and this solution was added the MetA in the proportions shown in Table 1. ACN polymerizes during the cure of the resins and, therefore, it is not necessary to remove it by evaporation.

Suspensions of NSP were prepared by mixing 1 g of a 3 wt% solution of $AgNO_3$ in ACN with the required amount of MetA. The viscosity of MetA is 5.7 Pa·s while that of ACN is $3.4 \cdot 10^{-4}$ Pa·s. Increasing the amount of NSP the proportion of BHT reducer agent present in the MetA decreases while the mobility of the reacting medium increases as a result of the increased proportion of the low-viscosity ACN.

It is well known that silver ions can react with some alkene molecules, in a reversible way, to form silver-alkene complexes (Hong et al., 2000; Zhang and Han, 2003). The interaction between Ag^+ ions with ACN is described as follows:

$$Ag^+ + 2\ H_2C{=}CHCN \rightleftharpoons \left[Ag\left(H_2C{=}CHCN\right)_2\right]^+$$

The reduction of silver ion by BHT is illustrated in the following reaction scheme:

$$\left[Ag\left(H_2C{=}CHCN\right)_2\right]^+ + H^\bullet \longrightarrow \left[\underset{\text{atomic}}{Ag}\left(H_2C{=}CHCN\right)_2\right] + H^+$$