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Development and characterization of the composites based on mesoporous MCM-41 and polyethylene glycol and their properties

Bahaa M. Abu-Zied [a,b,*], Mahmoud A. Hussein [a], Abdullah M. Asiri [a,b]

[a] *Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia*
[b] *Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia*

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ABSTRACT

Novel MCM-41/polyethylene glycol composites have been synthesized using different ratios of MCM-41. The structure of the different composites was confirmed by using various characterization tools, including: thermal analyses (TGA and DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and field emission scanning electron microscopy (FE-SEM). The XRD and FT-IR results indicated that PEG interacts with MCM-41 via the formation of hydrogen bonds where no new phase was detected. The TGA analysis results demonstrated that the presence of MCM-41 practically affects the temperature of the main step of degradation. The DTA analysis demonstrated that an increase in the MCM-41 content up to 30 wt.% is accompanied by a continuous decrease in the melting point of PEG.

1. Introduction

During the last two decades, polymer-based organic–inorganic composites have received world-wide attention in the field of material science. This attention is because the resultant materials may offer superior performance, such as mechanical toughness for engineering resins, permeability and selectivity for gas/liquid separation, and thermoelectric effect for electronics [1–3]. Such superior performance is attributed to the synergy between the inorganic particles and the polymer matrix in which they are dispersed [4]. Polymers can be reinforced by particles of several materials including precipitated silica [5], titania [6], and zirconia [7].

The material MCM-41 belongs to a group of mesoporous materials known as M41S which was first reported by researchers of the Mobil Research and Development Corporation in 1992 [8–10]. MCM-41 is characterized by the following: a one-dimensional, hexagonally ordered pore structure; a high specific surface area and a pore volume of approximately 1000 m^2/g and 1 cm^3/g, respectively; very narrow pore size distribution; tunable pore size between 1 nm and 10 nm or more depending on the choice of surfactant, auxiliary chemicals and reaction conditions; adjustable hydrophobicity; easy pathway of preparation with negligible pore-blocking effects and very good thermal stability [8–11]. Due to these unusual characteristics, the mesoporous MCM-41 material has recently been extensively utilized as an effective reinforcement filler to enhance the physico-chemical properties of many polymers. Epoxy–resin/MCM-41, polypropylene/MCM-41 and polyethylene/MCM-41 composites with enhanced thermal stability and mechanical properties have been reported [12–14].

Phase change materials (PCMs), which can absorb/release high latent heat during the melting/solidifying process, have received attention recently. In general, polyethylene glycol (PEG) is considered to be a promising PCM owing to its suitable phase change temperature, high latent heat capacity, congruent melting, non-toxicity, chemical stability, lack of super cooling, low vapor pressure, little to no volume change during the solid–liquid phase change, high thermal and chemical stability after long-term utility period and low-cost [15–17]. When PEG is used as a PCM for thermal energy storage, its molecular weight is a key issue for its application as a thermal energy storage material [15]. The molecular weight is crucial because both the melting point and the fusion heat of PEG depend on it. However, only low-molecular-weight PEG has been used as a phase change heat storage medium. This type of PEG belongs to the category of classical solid–liquid phase change substances, and thus it cannot be stored in conventional storage tanks, but must be packaged in specially sealed containers to prevent its leakage in the melting state [18]. In addition, PEG can be incorporated directly into porous materials.

In the open literature, there are only a few reports regarding the MCM-41/PEG composite. Accordingly, the present investigation seeks to obtain new materials with several property modifications by adding MCM-41 mesoporous materials to polymeric matrices using a simple solution method. Several tools were employed to

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[*] Corresponding author at: Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia. Tel.: +966 563737563; fax: +966 2 6952292.

E-mail addresses: babuzaid@kau.edu.sa, babuzied@yahoo.com (B.M. Abu-Zied).

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characterize and verify the properties of the obtained composites. These tools include thermal analyses (TGA and DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and field emission scanning electron microscopy (FE-SEM).

2. Experimental

2.1. Materials

Polyethylene glycol with average molecular weights of 6000 was purchased from Aldrich Chemical Co. and was used without further purification. Ethyl acetate (analytical grade) was obtained from Merck, and was also used without further purification as the solvent in the composites preparation.

2.2. Preparation of mesoporous MCM-41 material

The parent MCM-41 was synthesized according the procedure similar to that reported by Grün et al. [19]. Briefly, 2.5 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 50 g of distilled water, and 13.5 g of aqueous ammonia (28 wt.%) and 60 g of absolute ethanol were added to the surfactant solution. The solution was stirred for 15 min (500 rpm) and 4.7 g of tetraethyl orthosilicate (TEOS) were added at one time resulting in a gel formation. After stirring for 2 h, the gel was aged for 1 h at room temperature, then filtered and washed with 300 ml of distilled water. After drying overnight at 90 °C, the sample was heated to 550 °C in air flow and kept at that temperature for 2 h, to remove the template then cooled to room temperature.

2.3. MCM-41/PEG composites preparation

The composites were prepared by adding 1 g of polyethylene glycol and increasing amounts of MCM-41 material (2–30 wt.%) in 20 ml of ethyl acetate under magnetic stirring at the speed of 600 rpm at 60 °C for 8 h. Next, the solvent was evaporated in Petri dishes for at least 24 h at room temperature and vacuum for 4 h (between 5 and 10 Torr). Similar procedure was reported recently for the preparation of polyethylene glycol and various mesoporous matrices composites [20].

2.4. Instrumentation

Powder X-ray diffractograms were recorded at 2θ values from 0.5° to 80° with a step of $0.02^\circ\,s^{-1}$ using a PANalytical (X'pert BRO, Holland) instrument with a Ni-filtered Cu Kα radiation source ($\lambda = 0.15418$ nm) operated at 45 kV and 40 mA. FT-IR spectra were recorded over the wavenumber range of 4000–400 cm^{-1} with the aid of the Smart iTR which is an ultra-high-performance, versatile Attenuated Total Reflectance (ATR) sampling accessory on the Nicolet iS10 FT-IR spectrometer. The simultaneous TGA and DTA curves were recorded with the aid of Shimadzu DT-60 instrument apparatus using a heating rate of 10°/min. The morphology of the samples was analyzed by field-emission scanning electron microscope (FE-SEM) on a JEOL model JSM-7600F microscope. The compositions were examined by energy-dispersive X-ray spectroscopy (EDX) coupled to the SEM.

3. Results and discussion

3.1. Structural properties of the MCM-41/PEG composites

To determine whether the composite formation affected the channel arrangements of the mesoporous MCM-41, the low angle X-ray technique was employed. The X-ray diffraction pattern of ordered mesoporous MCM-41 is well known to exhibit a strong peak in the 2θ range of 1.8–2.8° due to the (100) diffraction lines and the weak peaks in the 2θ range of 3.5–4.8° and 5.6–6.7° are attributable to the (110), (200) and (210) reflections, which indicate the formation of a well-ordered hexagonal lattice of MCM-41 materials (space group p6mm) [21–25]. The low angle XRD diffractogram of the purely siliceous MCM-41 material, shown in curve a in Fig. 1, reveals the existence of a strong peak (100) at $2\theta = 2.18^\circ$ together with two weak peaks at 3.84° and 4.46° ascribed to the (110) and (200) crystal faces, respectively. A very weak (210) reflection is also present, as indicated by the peak appearing at $2\theta = 5.9^\circ$. This result shows that the MCM-41 synthesized in this study possesses a highly ordered hexagonal mesostructure [21–27]. For the various MCM-41/PEG samples, indicated by the curves b–g in Fig. 1, the (100) peak intensity is sharply decreased, broadened and shifted slightly to a higher angle. Meanwhile, the other peaks almost disappeared. This phenomenon has been reported previously. For instance, Li et al. [26] have observed an intensity decrease of the (100) peak characterizing the MCM-41 material together with the disappearance of other peaks, (110) and (200), for the 13.21 wt.% Fe–MCM-41 sample; hence, they concluded that the mesoporous symmetry was reduced by the introduction of an excess of iron atoms. In another study by Atchudan et al. [21], they also reported the same trend of decreasing (100) intensity for chromium containing MCM-41; moreover, they noted the broadening and a shift to higher 2θ values of the diffraction peak with the increase in the Cr concentration. Similar findings were reported for calcium, iron, cobalt, nickel and titanium-incorporated MCM-41 samples [22–25,27].

Feng et al. [20] have prepared PEG composites with different mesoporous matrices (AC, SBA-15 and MCM-41) by a direct blending and impregnating method. Their XRD low angle diffraction pattern of PEG/MCM-41, 70 wt.% PEG, composite revealed poorer crystallinity compared to pure MCM-41, where most of the reflections, even the (100) peak, disappeared. In our case, the (100) reflection still persists, even when using a higher PEG content than that reported by Feng et al. [20]; this difference could be due to the

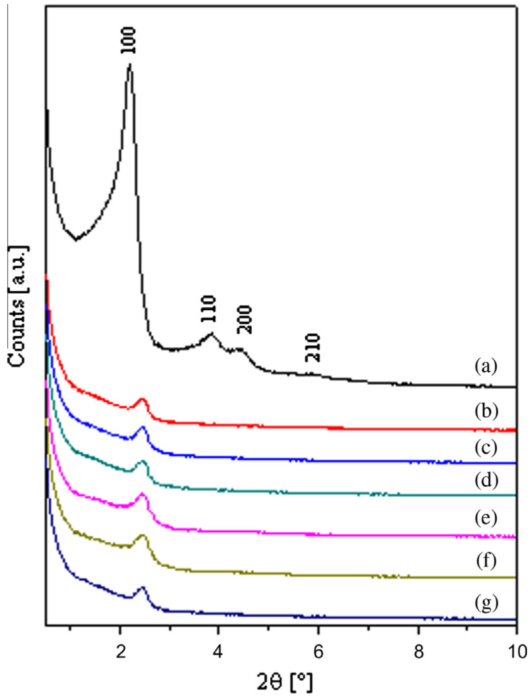

Fig. 1. Low angle XRD patterns obtained for neat MCM-41 (a), MCM-41/PEG 2 wt.% (b), MCM-41/PEG 5 wt.% (c), MCM-41/PEG 10 wt.% (d), MCM-41/PEG 15 wt.% (e), MCM-41/PEG 20 wt.% (f), and MCM-41/PEG 30 wt.% (g).