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Influence of mesoporous silica and hydroxyapatite nanoparticles on the mechanical and morphological properties of polypropylene

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ABSTRACT

This paper presents the effect of different types of additives on the morphology and mechanical performance of polypropylene (PP). Three different types of nanoparticles, containing mesoporous silica (MCM-41), Hydroxyapatite (HA) and the composite of MCM-41 and HA (MH) were used. Nanocomposites containing PP, 3 wt.% of maleic anhydride grafted polypropylene (PP-g-MA) and 3 wt.% of different nanoparticles were prepared using the melt-compounding technique in a twin-screw extruder. The bulk mechanical response of the nanocomposites such as tensile, flexural and Izod impact properties were studied. The results of mechanical tests show that at the same nanomaterial content, all the nanofillers cause better tensile, flexural and impact strength than neat PP. The MH nanoparticle improves the mechanical properties of PP, better than the other nanoparticles because this nanofiller contains good properties of both MCM-41 and HA nanoparticles in itself. In order to investigate the effect of foam agent on the mechanical properties of neat PP and nanocomposites based on PP, inorganic azodicarboxamide was added to the aforementioned mixtures as chemical blowing agent and the foamed specimens were resulted using the melt-compounding technique. The results reveal that addition of foam agent to mixtures, leads to increase the flexural characteristics of samples, but the tensile properties and impact strength decrease. Scanning electron microscopy (SEM) was used to assess the fracture surface morphology and the dispersion of the nanoparticles. X ray diffractometry (XRD) was used to examine the intercalation effect on the nanocomposites. The observations show that the nanomaterials were well dispersed in the polymer matrix and the enhancement of the interface between the matrix and fillers was obtained by the incorporation of MH, MCM-41 and HA nanoparticles into PP matrix.

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1. Introduction

The hybrid organic–inorganic nanoscale composites have received special attention, both in industry and in academia, because of their improved properties at very low content levels compared with conventional filler composites. They often improved the properties such as mechanical, dimensional, thermal stability with respect to the bulk polymer [1]. One of the most promising composites is the hybrid based on organic polymers such as polypropylene (PP) and inorganic nanofiller such as mesoporous silica.

In recent years PP nanocomposites have attracted great interest in academia researches. The attractiveness of this class of material lies in the large improvements in both mechanical and thermal properties.

The mesoporous silica nanofillers have received much attention due to their ordered structure, high surface area and easiness for functionalization of the nanopores [2]. Recently, the papers about increasing the mechanical and thermal properties of polymeric matrix by adding the mesoporous particles are published [3–6]. Wang et al. have investigated the effects of MCM-41 on the tensile properties of PP [7,8] and they showed that the tensile strength for 3 wt.% structure is approximately 6% greater than neat PP. Also they demonstrated that nanocomposites of PP, PP-g-MA and MCM-41 have higher impact strength with respect to neat PP [9].

Low hydrothermal stability of MCM-41 nanoparticles undoubtedly limits their application, which is thought to improve by increasing the thickness of the pore walls and/or by enhancing the local ordering of the walls [10]. In the other hand, combining two nanomaterials with different shapes may generate more effectively enhanced effect due to the expected synergistic effect. For example, Wang et al. showed that nanocomposites of PP/MCM-41/MMT have higher values of tensile strength, tensile modulus and impact strength than PP/MMT and PP/MCM-41 nanocomposites [11]. Therefore, by combining mesoporous silica with a rigid rod shape nanoparticle such as Hydroxyapatite can enhance the pore walls and achieve higher mechanical performance.

Hydroxyapatite (HA), is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$, but is usually written $Ca_{10}(PO_4)_6(OH)_2$ to denote that the crystal unit cell

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comprises two entities. HA the major inorganic component of bone mineral, has been used for various biomedical applications such as implant coating [12]. The mechanical strength of polymers can be greatly improved by adding a small amount of these nanofillers. Mechanical properties of microscale polymer composites reinforced with HA have been studied in several studies. The flexural behavior of PP filled with 40 vol.% HA microparticles was studied by Bonfield and coworkers [13]. Liu and Wang investigated the mechanical properties of injection molded PP composites filled with 10–25 vol.% HA particles (24.5 μm) [14]. Younesi and Bahrololoom studied the effect of molecular weight and particle size on mechanical properties of PP/HA biocomposites [15]. Furthermore, they investigated mechanical properties of PP–HA composites and applied temperature and pressure at hot pressing process in another study [16]. Very recently, Li and Tjong introduced nano-sized HA into PP and demonstrated that the addition of 8 wt.% HA, leads to the increase of the tensile modulus by nearly 25% [17]. Their mechanical measurements showed that HA stiffened and reinforced PP but reduced its tensile ductility and impact strength considerably.

The combination of functional nanoparticles and polymer foaming technologies has generated a new class of materials known as nanocomposite foams. Those materials exhibit enhanced thermo-mechanical properties as a result of the multifunctional role played by nanoparticles in such systems. Nanofillers act as nucleating agents for bubble formation promoting improved cell morphology which at the same time lead to an overall increase in macroscopic properties [18]. Many studies on polymer nanocomposite foams have used CO_2 as a blowing agent. However, there is lack of information about the polymer nanocomposite foams prepared by chemical blowing agents. Chemical blowing agents are added to the thermoplastic melt or thermoset monomer; then the temperature is elevated causing decomposition into residual material and gas, forming of foam. Two basic steps are involved in the foaming process: bubble nucleation and growth. Nucleation is the process in which a new phase (bubble phase) is generated from the initially homogeneous polymer–gas mixture. Growth is the process in which bubble nuclei grow into final bubbles. A few investigations have analyzed the mechanical properties of nanocomposite foams produced by using chemical blowing agents. The mechanical properties of nanocomposite foams can vary widely depending on nanofillers, but in general, they have good compressive strength, but poor tensile and impact strength. Saiz-arroyo et al. showed that nanosilica particles act as effective nucleating agents, improving compressive strength of low density polyethylene [18]. Kord et al. investigated the tensile properties of high density polyethylene/wood flour/nanoclay composites [19]. They showed that by adding chemical foaming agent to the composites, the tensile modulus decreases. Farsheh et al. [20] showed that the tensile strength of wood plastic/MWCNT composites reduces by foaming, regardless of the CNT content. But the tensile strength of sample containing nanoparticles increases due to high aspect ratio and large surface area of CNTs. When compared with the neat polymer that comprises the matrix, they can have higher modulus [21–23] while reducing weight. Taking advantage of the low weight and high compressive strength, one of the first applications for nanocomposite foam was as buoyancy aids in deep-sea structures [24,25]. They have also found additional applications in the aerospace industry as a lightweight filler [26].

In this study, in order to enhance the pore walls of MCM-41, hydroxyapatite was combined with MCM-41. MCM-41/HA nanocomposite (MH) is a new nanocomposite which is proposed in this research and has reinforced PP to achieve the better mechanical properties. PP nanocomposites reinforced with MCM-41, HA and MH nanocomposite were prepared by means of extrusion and injection molding. Maleic anhydride-grafted PP (PP-g-MA) was introduced into the system as a compatibilizer to improve the adhesion between the PP and nanoparticles. Moreover, inorganic azodicarboxamide was added to the nanocomposites as a foam agent to investigate the foaming behavior. The purpose of this paper is to study and compare the morphology and mechanical properties of different polymeric hybrid nanocomposites and their foam's structure.

2. Experimental details

2.1. Material

Polypropylene homopolymer (PP 570P), in pellet form, was obtained from Sabic company (Saudi Arabia) with the following characteristics: Melt Flow Index (MFI) = 8 g/10 min (230 °C/2.16 kg) and density = 905 kg/m³. The monodisperse nano-sized MCM-41, HA and MCM-41/HA nanoparticles were synthesized in our lab. The nano-sized mesoporous particles were prepared in an aqueous phase by sol–gel method. Materials used in this study were $CaCl_2 \cdot 2H_2O$ (Merck, 99–102%) and $K_2HPO_4 \cdot 3H_2O$ (Merck, ⩾99%), as phosphorous and calcium sources, respectively. Cetyltrime thylammonium bromide (C16TAB-Sigma) as template, tetraethoxysilane (Merck, ⩾99%) as silicon source and ammonia solution (25% Merck, >98%) as pH controller were also used. Next, tetra-n-botyl-ortho titanat as titanium source, ethanol and diethanolamine were used for preparation of Titania sol. Moreover, polypropylene grafted maleic anhydride (PP-g-MA) with MFI = 2 g/10 min from Karangin company (Iran) was employed as compatibilizer. PP-g-MA contains 1.7 wt.% of maleic anhydride (MA). Foam agent used in this study was azodicarboxamide ($C_2H_4N_4O_2$) (Merck, ⩾98%) with density of 1.87 g/cm³ and melting point of 220–225 °C.

2.2. Synthesis

2.2.1. Synthesis of hydroxyapatite
$K_2HPO_4 \cdot 3H_2O$ was first dissolved in 100 ml of deionized water. Then, $C_{16}TAB$ was added under magnetic stirring (500 rpm). After that, enough amount of TMAOH was added to adjust pH at 12. In parallel, in another container $CaCl_2 \cdot 2H_2O$ was also dissolved in 100 ml deionized water and then, it was added to the former solution under constant stirring (500 rpm). The obtained gel was aged at 30 °C for 30 h under reflux and static conditions after 1 h of stirring.

2.2.2. Synthesis of MCM-41 and MCM-41/HA (MH) composite
After the preparation process of HA, 45 ml TEOS was added drop wise to the solution under vigorous stirring (about within 30 min). The final solution was aged at 100 °C for various times of 0, 24, 36 and 48 h without stirring. The nominal composition is 60 wt.% of SiO_2. The solid products were filtered, washed and dried for 2 h at 90 °C. In the next step, they were calcined at 550 °C for 6 h and finally labeled as MH. For comparison, Pure MCM-41 was obtained by this procedure without the addition of $CaCl_2 \cdot 2H_2O$ and $K_2HPO_4 \cdot 3H_2O$ at 100 °C for 24 h [27,28].

2.3. Preparation of nanocomposites and nanocomposite foams

Prior to the preparation of the specimens, nanoparticles, PP-g-MA and PP were dried in a vacuum oven for 48 h at 80 °C. In order to improve the nanoparticles dispersion in PP matrix, 3 wt.% PP-g-MA was added to each combinations. PP, PP-g-MA granules, 1 wt.% of foam agent – in the foamed specimens – and 3 wt.% of different nanoparticles were melt-compounded in a Brabender twin-screw extruder (DSE 25) with 25 mm diameter screw and length to diameter (L/D) ratio of 40. The screw speed was fixed at 100 rpm and