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Production of PVC/α-MnO_2-KH550 nanocomposite films: Morphology, thermal, mechanical and Pb (II) adsorption properties

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ABSTRACT

α-MnO_2 nanorods have been synthesized through a simple method without the presence of catalysts and templates. The prepared nanorods were employed as fillers to retrofit and increase the mechanical strength, thermal stability and adsorption properties of poly (vinyl chloride) (PVC) as one of the most important thermoplastics. To prevent accumulation and increase compatibility of α-MnO_2 with the organic PVC matrix, the nanorods were modified with γ-aminopropyltriethoxy silane (KH550). Nanocomposites (NCs) were prepared with different amounts of modified α-MnO_2 nanorods (1, 3 and 5 wt%). FE-SEM and TEM characterization revealed that the α-MnO_2 nanorods are in rod-like morphology with diameter of 40 nm and uniformly dispersed in the PVC matrix. Optical behavior, thermal stability, tensile and self-extinguishing properties of the obtained NCs was studied, respectively. Removal of Pb(II) ion from aqueous solution by NCs was also performed through the flame atomic adsorption spectroscopy analysis. The results indicated that PVC/α-MnO_2-KH550 NCs exhibit better thermal stability, tensile and self-extinguishing properties than pure PVC in three weight percent. The obtained results of adsorption revealed that the NC films could be used for the removal of Pb(II) ions from the aqueous medium.

1. Introduction

Polymer-Metal nanocomposites (PMNCs) are discussed as a group with perspective physical and chemical properties, since they possess interesting properties of both components. In fact, NCs with nanoscale fillers produce versatile polymer composites with enhanced mechanical, electrical, optical, thermal and magnetic properties. For this reason, these NC mate-

Abbreviations: PVC, poly(vinyl chloride); NCs, nanocomposites; FAAS, flame atomic adsorption spectroscopy; NP, nanoparticles; FTIR, Fourier transform infrared spectroscopy; XRD, X-ray diffraction; TGA, thermogravimetric analysis; TEM, transmission electron microscopy; FE-SEM, field emission scanning electron microscopy; KH550, aminopropyltriethoxy silane coupling agent; R^2, correlation coefficient.

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rials are extensively used for wide applications in catalysis, packaging, plastics and rubber reinforcement, automobile industry, electronics, biotechnology, etc. [1–5].

Poly(vinyl chloride) (PVC) is one of the most widely investigated polymers. It exhibits excellent chemical resistance and workability, relatively low cost and biological activity. Because of its properties, PVC has found potential for many applications in healthcare, construction, electric cables, clothing and furniture. It is accepted that, the PVC has low thermal stability and is brittle. To improve these limitations and achieve desired properties, nano-fillers should be uniformly distributed in polymer matrix [6,7]. Transition-metal oxide nanostructures (MONSs) have been considered for the unexampled excellent performances and the various good properties [8–10]. Therefore, they are good choices for preparation of NCs as filler materials. Among effective candidates, manganese dioxide (MnO_2) has been of specific interest and was extensively investigated. MnO_2 exists in several crystallographic structures (such as α, β, γ and δ). These structures differ in that the fundamental unit [MnO_6] octahedral linked in different ways. α-MnO_2 exhibits a special tunnel structure (2 $\times$ 2 tunnel structure) that is manufactured from double chains of [MnO_6] octahedral [11–12]. MnO_2 finds application in many fields because of its specific physical and chemical properties such as high abundance, low cost, high surface area, adsorption abilities, good stability under acidic conditions and environmental benignity [13–16]. These good features will ultimately enable NCs based on MnO_2 to serve as materials for lithium ion batteries alkaline and rechargeable batteries [17–19], alternative electrode materials for supercapacitors due to their ultrahigh theoretical capacitance [20–22], wastewater treatment due to their special tunnel structure [23–25], molecular/ion sieves [26,27] and catalysts because of their ability to oxidation [28,29]. Embedment of nanoparticles (NPs) into the polymer matrix has some drawbacks. The main problem for the preparation of the polymer NCs is the incompatibility of metal oxides with organic polymers and aggregation between NPs. Accordingly, it is difficult to produce monodispersed NPs in the polymer matrix [30–32]. The surface modification of NPs by chemical treatments such as applying silane coupling agents is a useful method to obtaining homogeneous dispersion in the matrix. Not only the modification prevents agglomeration but also improves mechanical performance of PVC [33]. Aminopropyltriethoxy silane coupling agent (KH550) with its special structure improves the hydrophobicity of nanofillers [34–36]. Ultrasonic irradiation employs to form dispersed phases. This technique helps to control size distribution and improvement of the NPs dispersion in the polymer matrix [37]. Researchers reported that PVC NCs and MnO_2 particles have the ability to remove heavy metal ions and organic contaminants due to the existence of good properties such as good physical and chemical stabilities and high surface area [25,38–40]. Accordingly, functional properties of the prepared NC films for the absorption of Pb(II) ion were investigated by flame atomic absorption spectrophotometer (FAAS). The special purpose of this study is fabrication and characterization of PVC/α-MnO_2-KH550 NC films embedded with various amounts of the modified α-MnO_2 nanorod and discussion about their mechanical, morphology, Pb(II) adsorption, thermal and self-extinguishing properties.

2. Experimental section

2.1. Materials

$KMnO_4$ (Sigma-Aldrich, Seelze, Germany) and THF (JEONG Wang, Korea) were used. Emulsion grade PVC (Mw: 78,000 g/mol) was purchased from LG Chem (Korea). The silane coupling agent, γ-aminopropyltriethoxy silane (KH550), manganese (II) sulfate monohydrate ($MnSO_4 \cdot H_2O$) and ethanol were supplied from Merck Chemical Co. (Germany). Lead (II) nitrate was purchased from Cica-Reagent (Tokyo, Japan).

2.2. Equipment

Fourier transform infrared (FT-IR) spectra (Jasco-680 spectrophotometer) were taken in KBr pellets to examine vibration bands and structures. Ultraviolet–visible (UV–Vis) spectra were recorded on JASCO, V-570 spectrophotometer. X-ray diffraction [Philips X'PERT MPD (Germany)] was used to identify the atomic and molecular structure. This technique was carried out using Cu Kα incident beam (λ = 1.51418 Å) in the range of 2θ: 10–80° and at a rate of 0.05°/min. Morphology of modified nano-fillers and NC films were studied by FE–SEM [HITACHI (S-4160)]. TEM analysis [Philips (CM 120, Netherlands)] was applied to examine fine details. Thermal analysis was performed by TGA instrument (STA503 TA) at a heating rate of 10 °C/min from 100 to 800 °C under argon atmosphere. Preparation of NCs was accomplished by Topsonics homogenizer ultrasonic liquid processors (IRI), with frequency wave of 25 kHz and power of 100 W. To search for tensile testing, the Testometric Universal Testing Machine M350/500 (UK) at a speed of 5 mm/min was used. Samples were prepared with dimensions of 35 mm $\times$ 9 mm with thickness of 40 μm. The adsorption percent of neat PVC and NC film 5 wt% for removing Pb (II) from neutral aqueous solutions at room temperature were considered by the Perkin-Elmer 2380-Waltham flame atomic absorption spectrophotometer (FAAS).

2.3. Synthesis of α-MnO_2 nanorods

α-MnO_2 nanorods were synthesized using a rational route [41]. 1 mmol of Manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, 0.2 g) and 2.5 of mmol Potassium permanganate (VII) ($KMnO_4$, 0.5 g) were mixed in the distilled water at the room temperature. The solution was taken into a Teflon-lined stainless steel autoclave and was heated for 12 h at 140 °C. The