



Research paper

Influence of sepiolite on thermal, mechanical and biodegradation properties of poly-3-hydroxybutyrate-co-3-hydroxyvalerate nanocomposites

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ABSTRACT

The clay polymer nanocomposites comprising of poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) and vinyl triethoxy silane grafted sepiolite (VTES-g-SEP) were prepared by the solution casting. Scanning electron micrographs revealed the absence of voids and high interfacial interaction between polymer and VTES-g-SEP. Thermal and mechanical properties of the clay polymer nanocomposites were significantly enhanced as compared to the PHBV. The scanning electron micrographs of clay polymer nanocomposite films subjected to soil burial showed formation of pits and agglomerates. Additionally, Fourier transform infrared spectra of clay polymer nanocomposite films buried in soil demonstrated a sharp decline in the intensities of IR peaks was found at 3617–3019 cm^{-1} (OH stretching), 1710 cm^{-1} (carbonyl stretching), 1365 cm^{-1} (symmetric bending of C–H vibrations), 1265 cm^{-1} (C–O stretching), 1165 cm^{-1} (asymmetric stretching of C–O–C group) and 978 cm^{-1} (C–H bending) after 90 days of soil burial. In a nutshell, the clay polymer nanocomposite films can be used in packaging applications.

1. Introduction

Synthetic plastics are extensively used in daily life. However, synthetic plastics are identified as main solid waste environmental pollutant due to their xenobiotic nature. On the other hand, biodegradable polymers received a great deal of interest globally over the last two decades. The polyhydroxyalkanoates (PHA) are biodegradable, biocompatible and non-toxic aliphatic polyesters. The PHA are obtained from renewable resources. The PHA are intracellularly synthesized by microorganisms as inclusion bodies under the conditions of nutrient stress (Masood et al., 2012) (Masood et al., 2015). Copolymerization of 3-hydroxybutyrate (3HB) units with 3-hydroxyvalerate (3HV) units results in the production of poly-(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), which represents the most widely studied member of the PHA family (Masood et al., 2011). The tailoring of PHA composition (ratios of 3HB vs. 3HV) depends upon the types of microorganism and carbon substrates used for fermentation (Aramvash et al., 2016) (Moorkoth and Nampoothiri, 2015). The introduction of 3HV units induces defects in the crystal lattice, thus making PHBV more flexible and crystalline. This is important for practical applications, especially for the packaging industry (Wang et al., 2016) (Weng et al., 2010). Poor mechanical strength and low thermal stability of PHBV are

also reported (Wang et al., 2016) (Rhim et al., 2013).

The addition of nanofiller with dimension less than 100 nm offers a novel approach to encourage the applications of biodegradable polymers in the packaging industries. Sepiolite is an important member of the phyllosilicate family. The structural formula of sepiolite is $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$. The sepiolite occurs in the form of bundles of thick fibers (100–5000 nm \times 10–30 nm \times 5–10 nm) (Benlikaya et al., 2009). The sepiolite fibers are made up of an octahedral layer of coordinated magnesium atoms sandwiched between the two layers of SiO_4 tetrahedrons silicate units (Shariatmadari and Mermut, 1999). The discontinuous longitudinal structure of silica sheets results into the formation of zeolitic channels with a cross-section of ca. $1.1 \times 0.4 \text{ nm}^2$ (Darder et al., 2006). The surface energy of sepiolite is about 240 mJ/m² (Aranda et al., 2008). The porosity and specific area of sepiolite is 0.4 cm³/g and 350 m²/g, respectively (Helmy and de Bussetti, 2008). Approximately 2.2 silanol groups (Si–OH)/100 Å² are present after every 0.5 nm on the surface of external channels of sepiolite (Hermosin and Cornejo, 1986). The coordinated water molecules surround the Mg (OH)₂ molecule in the channels under ambient environmental conditions. The zeolitic water molecules in the internal channels cannot be replaced by molecules of low polarity and larger size. However, the polar molecules are easily adsorbed on sepiolite, this accounts for an

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Table 1
Compositions and codes of all systems.

S. No.	PHBV (wt%)	PEG (wt%)	VTES-g-SEP (wt%)	Identification codes
1	100	0	0	PHBV
2	77	18	3	PHBV-3
3	76	18	5	PHBV-5
4	74	18	7	PHBV-7

40–50% of its whole surface area (Galan, 1996). Sepiolite has been used to improve thermal and mechanical properties of high density polyethylene (Pratap Singh et al., 2016), chlorinated polyethylene/ethylene methacrylate copolymer (Bhagabati et al., 2015), polylactic acid/calcium carbonate (Sabzi et al., 2013), linear low density polyethylene (Shafiq et al., 2012) and polyamide 6 (García-lópez et al., 2010). Sepiolite has recently gained an increasing popularity for making clay polymer nanocomposites due to its easy availability and low price. The substantial improvement in thermal, mechanical and barrier properties of clay polymer nanocomposites is achieved by loading a small quantity of nanoclay and depend upon the high aspect ratio and large interface between nanofiller and polymer (Arrieta et al., 2015) (Rhim et al., 2013)(Carli et al., 2011) (Xie et al., 2009). However, it is difficult to attain the uniform dispersion of sepiolite fibers within the polymeric matrix due to its occurrence in the form of bundles. Therefore, an organic modification of sepiolite with a silane coupling agent is a promising approach to ensure the good interfacial interaction between polymer and sepiolite (Shakil et al., 2017). Previously, the PHA based clay polymer nanocomposites have been developed using Tungsten disulphide inorganic nanotubes (Naffakh et al., 2014), montmorillonite Cloisite30B (Farmahini-Farahani et al., 2015), cellulose nanowhiskers (Martí et al., 2014), carbon nanotubes (Shan et al., 2011), halloysite (Carli et al., 2011) and silica nanofibers (Xie et al., 2009).

This paper describes the first attempt to study the influence of functionalized sepiolite on the structural and physiochemical properties of PHBV. The pristine sepiolite was modified with vinyl triethoxy silane (VTES) using an ex-situ silanation method. Fourier Transform Infrared spectroscopy, wide angle X-Ray diffraction analysis, thermogravimetric analysis and differential scanning calorimetry were used for characterization studies of clay polymer nanocomposite films. Mechanical properties were determined. It was also investigated whether there was any influence of VTES grafted sepiolite on biodegradation properties of the clay polymer nanocomposite films.

2. Materials and methods

2.1. Materials

PHBV synthesized by *Bacillus cereus* was used. Sepiolite (SEP), vinyl triethoxy silane (VTES), and polyethylene glycol (PEG, Mw = 400 g/mol) were obtained from Sigma-Aldrich Chemie, Steinheim, Germany. All other materials were used as such without further purification.

2.2. Preparation of VTES-g-SEP

SEP (10 g) was dissolved in water (1 L) and stirring was continued for 24 h. Then SEP was filtered and dried in a vacuum heating oven. The purified SEP was dispersed in 300 mL isopropanol and VTES (12 g) was added. The mechanical mixing was continued for two hours. The resulting solid was recovered by filtration and washed with methanol (60 mL). This VTES modified (ex-situ) sepiolite (VTES-g-SEP) was dried overnight under vacuum at 50 °C.

2.3. Preparation of nanocomposite films

The nanocomposite films were prepared by the solution-casting method. Briefly, PHBV, PEG and VTES-g-SEP were dissolved in chloroform by sonication using ultrasonic bath cleaner for one hour. The mixture was poured in a petri-dish and allowed to evaporate at room temperature. The compositions and codes of all systems used in this study are given in the Table 1. The reactions of VTES with the pristine sepiolite, PHBV and PEG are shown in Fig. 1.

2.4. Characterization studies

2.4.1. Scanning electron microscopy (SEM)

The morphologies of the nanocomposite films were evaluated by SEM (Joel, Japan). The cryo-fractured samples were coated with gold prior to observation.

2.4.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was performed using a Nicolet 6700 FTIR spectrophotometer (Thermo Electron Corp, Marietta, OH). The spectra of samples were obtained using attenuated total reflectance mode with a diamond crystal in the range from 4000 to 400 cm⁻¹.

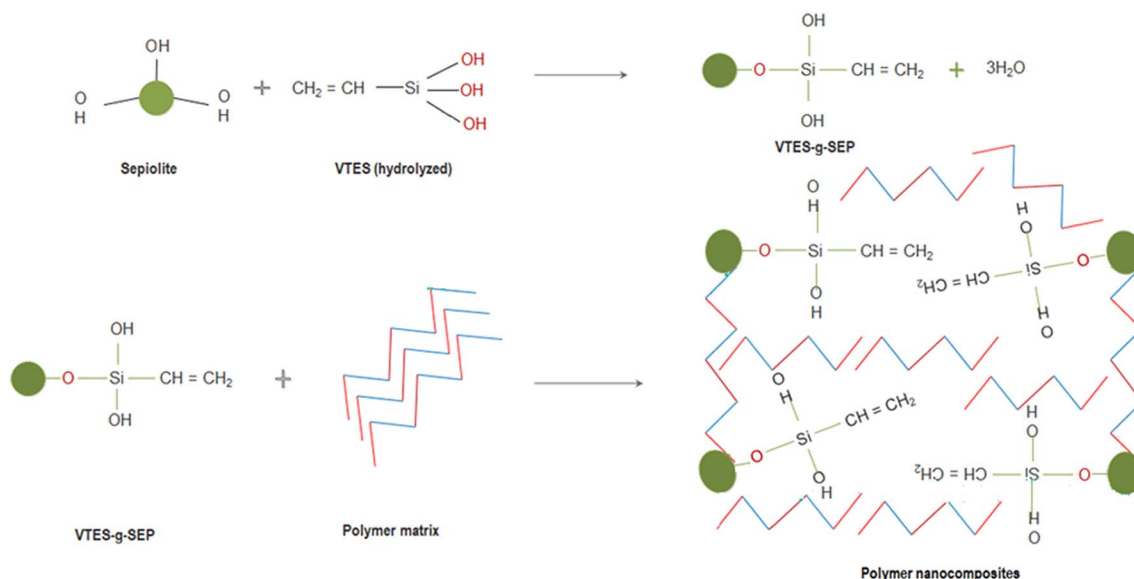


Fig. 1. A possible scheme of chemical reactions during the synthesis of PHBV/sepiolite nanocomposites.

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