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Optimization of mechanical and color properties of polystyrene/nanoclay/nano ZnO based nanocomposite packaging sheet using response surface methodology

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A B S T R A C T

In this study, a new interesting ternary nanocomposite based on polystyrene (PS), nanoclay and zinc oxide nanoparticles (ZnO) has been suggested as a food packaging material. Effects of ZnO (0–2 wt%) and organoclay (Cloisite® 15 A) nanoparticles (0–7.01 wt%), on mechanical and color properties of the general purpose polystyrene (GPPS) sheets were quantitatively investigated using the response surface methodology (RSM). The structural features and surface morphology of resulted nanocomposites and the dispersion quality of nanoparticles in the polymer matrix were studied by scanning electron microscopy (SEM(and X ray diffraction (XRD) analysis. SEM and XRD results showed that the presence of ZnO nanoparticles improved the distribution of organoclay (OC) in the GPPS matrix and vice versa. Regression models were developed for ultimate tensile strength (UTS), strain at break (SB), Young's modulus (YM), lightness (L) inedx, yellowness index (YI) and whiteness index (WI) as a function of ZnO and organoclay concentrations. Linear and quadratic terms of regression models showed a significant influence on the UTS. In the case of L index, the linear term of organoclay and for SB, linear terms of both nanoparticles effects were significant. The optimized variables were found to be 0.81% ZnO and 0.57% organoclay for a maximum desirability of 0.805.

1. Introduction

The general purpose polystyrene (GPPS) is one of the most widely used thermoplastic polymers in various industrial segments including food packaging industry. Due to its high stiffness, strength, durability, good thermal properties, low moisture absorption, transparency, light density, convenience of processing and molding, and low cost, this polymer is widely used as a food packaging material (Bilgiç & Karakehya, 2016; Junior, Soares, Luetkmeyer, & Tavares, 2014; Praseetha, George, & Jayakrishnan, 2017; Xue et al., 2017). One major disadvantage of polystyrene is its brittleness, which limits the engineering applications of this material (Scheirs & Priddy, 2003). It is also one of the largest environmental pollutants, due to its resistance to microbiological degradation.

The intense use of polymeric materials combined with their enormous stability has created serious problems of plastic waste and has given rise to an intensive interest in new polymer systems, such as oxo-biodegradable materials (Nakatani & Miyazaki, 2013; Nakatani, Motokucho, & Miyazaki, 2015). The oxo-biodegradation involves two stages, abiotic and microbial oxidation. The abiotic oxidation of polymers can be catalyzed by pro-oxidants and photocatalysts such as ZnO (Ammala et al., 2011: Bandyopadhyay & Basak, 2007). Researchers reported that in the second stage of oxo-biodegradation, biodegradation occurs only on the surface of polymer not in the bulk volume, probably due to the inaccessibility of oxidation products to microorganisms (Bonhomme et al., 2003) and suggested that montmorillonite nanoclay have used along with a pro-oxidant to improve the overall oxo-biodegradation of polymers (Reddy, Gupta, Gupta, Bhattacharya, & Parthasarathy, 2008). There are published reports available on the photo degradation of PS/ZnO-NPs (Bandyopadhyay & Basak, 2007), whereas to the best of our knowledge, to date, there is no specific study on the oxo-biodegradation of PS/OC/ZnO-NPs system.

In recent decades there has been a considerable interest in using of polymer nanocomposites in food packaging, both in academic and

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industrial communities (Pasquale & Pollicino, 2017). Nanocomposite is a multiphase material in which 1, 2 or 3 dimension(s) of one of the phases are less than 100 nm (Liu & Xu, 2016). These systems have the potential for unique optical, thermal, barrier, and mechanical performance that far exceed that of conventional composites (Akelah, Rehab, Abdelwahab, & Betiha, 2017).

Among various nanoparticles, montmorillonite (MMT), as an abundant natural clay mineral with its unique structure and properties, has been extensively used in industrial applications (Xue et al., 2017). It is necessary to modify the nanoclay (NC) organically in order to increase the affinity with the hydrophobic polymer matrix (Pasquale & Pollicino, 2017). Organic clay (OC) materials are widely used in this regard and PS/OC nanocomposites have been extensively studied by scientists in recent years (Bilgiç & Karakehya, 2016; Giannakas, Spanos, Kourkoumelis, Vaimakis, & Ladavos, 2008; Kaya, Kaynak, & Hacaloglu, 2016; Liu & Xu, 2016; Remili, Kaci, Benhamida, Bruzaud, & Grohens, 2011; Suresh et al., 2017; Yang, Manitiu, Kriegel, & Kannan, 2014). These studies have shown that incorporation of NCs into polymeric matrices can improve their physical, thermal, mechanical and other properties.

Zinc oxide nanoparticle (ZnO-NP) is another nanomaterial that has gained significant research interest due to its low cost, abundance, eco-friendliness, high chemical and thermal stability, non-toxicity, and good UV absorbance properties (Ahmeda, Arfata, Al-Attara, Aurasb, & Ejaz, 2017; Hooda et al., 2017; Noshirvani, Ghanbarzadeh, Rezaei Mokarram, & Hashemi, 2017). Introduction of ZnO-NPs into polymer matrices can modify their mechanical, optical, electrical, barrier properties (Ahmeda et al., 2017; Hooda et al., 2017; Jassim, Alwan, Kadhim, & Nsaif, 2016; Ma, Chen, & Kuan, 2005, 2006).

In addition to polymer degradation, it is desired that the added nanoparticles have an improvement effect on the physiccal properties) such as mechanical properties(of the polymer. In the presence of two nanoparticles, synergistic or inhibitory effects on mechanical properties can be raised. From the viewpoint of mechanical properties, a well-dispersed and uniformly mingled microstructure of nanocomposites is highly desired. In recent years, some studies have reported synergistic effects of nanoparticles in polymer matrices (Deka, Baishya, & Maji, 2014; Jafarzadeha et al., 2017; Rostampour, Sharif, & Mouji, 2017; Tsotetsi, Mochane, Motaung, Gumede, & Linganiso, 2017). To our knowledge, however, few research studies on the synergistic effects of ZnO with NC/PS systems have been reported. Very recently, Han et al. (2016) reported the synergistic effects of microneedle like ZnO in a PS/organo-montmorillonite (OMMT) system obtained by melt mixing. These researchers reported a synergistic effect between OMMT and micro-size ZnO particles and stated that this resulted in improvements in the flame retardancy and dynamic mechanical properties in the PS/OMMT/ZnO. Photoactivity of metal oxides such as ZnO depends on size and surface to volume ratio of the particles, and the nanometer-size particles significantly increase the photo degradation efficiency compared to micrometer-size ones (Zan, Tian, Liu, & Peng, 2004). Since no study has been published on microstructure and mechanical properties of PS/OC/ZnO-NPs system and since the mechanical properties of polymers is the fundamental property needed to be optimized before they can exhibit their major useful service properties (Liu & Liang, 2011; Liu, 2011) in this study we investigated this properties.

Response Surface Methodology (RSM) is a method of design of experiments that is useful for modeling and analysis of problems in which the response is influenced by several variables and it can be used for optimizing the response (Bezerra, Santelli, Oliveira, Villar, & Escaleira, 2008; Zare, Garmabi, & Sharif, 2011). Utilizing RSM in optimization gives a more accurate and complete data with a minimal number of experiments (Chieng, Ibrahim, & Wan Yunus, 2012).

In this study, we developed the interesting ternary nanocomposites based on PS, PS/OC/ZnO-NPs, for using in food packaging purposes. Microstructure of the resulting nanocomposites was studied by XRD and SEM methods. The aim was to investigate the distribution of ZnO-NPs and OC in the ternary nanocomposites and the interaction effects of two nanoparticles on mechanical and color properties as two important physical properties and to find optimum concentration levels of two nanoparticles.

2. Material and methods

2.1. Material

Polystyrene granules (GPPS grade 1540), melt flow index (MFI) = 11 g/10 min were obtained from Tabriz Petrochemicals Industries Co. (Tabriz, Iran). The organically-modified clay (OMMT) containing dimethyl di-hydrogenated tallow alkyl ammonium ion, Cloisite® 15 A (C15A), was provided by Southern Clay Products Co. (USA). Hydrogenated tallow alkyl chain consists of 65 wt % of C_{18}, 30 wt % of C_{16}, and 5 wt % of C_{14}. The cation exchange capacity (CEC) of this clay was 125 meq/100 g clay. Zinc oxide nanoparticles powder (ZnO-NPs, > 99% pure, particle size 10–30 nm) was obtained from US Research Nanomaterials Inc. (Texas, USA). Other chemicals were analytical grade and provided from Merck Co. (Germany).

2.2. Preparation of nanocomposites

In this work melt-mixing was used for preparation of nanocomposites. The PS (powdered), C15A and ZnO-NPs were dried in a vacuum oven at 60 °C for 24 h and were premixed. For preparing samples, at first a master batch of PS and C15A or ZnO-NPs in a weight ratio of 4 (PS) to 1 (nanoparticle) were prepared using an intensive mixer with two counter-rotating roller rotors and 55 cm^3 capacity (Brabender, Germany) at 50 rpm rotor speed with a temperature of 200 °C and time of 10 min. The obtained master batch was pelletized, dried at 60 °C under vacuum for the subsequent 24 h. Polymer nanocomposites were prepared by diluting the master batch with PS using Brabender type mixer. The mixing temperature was 200 °C, the speed of rotation was 50 rpm and the mixing time was 5 min. Virgin PS was also processed in the mixer using the same procedure. Then the mixture was comminuted into pellets and the sheets were prepared by compression molding of pellets in a hydraulic press as follows: 5 min at 200 °C and no pressure, 5 min at 200 °C and 6 MPa, water cooling of molds down to room temperature keeping the pressure, mold opening and samples extraction, which were subsequently cut into suitable size for various analyses. The thickness of the sheets were controlled by the mold. The sheets obtained were 500 μm thick. We used a mold with normalized sample dimensions for tensile test according to ASTM Standard D638 (2010).

2.3. Physicochemical characterization

2.3.1. Dynamic light scattering (DLS)

Size distribution was determined using a Nano ZS (ZEN3600, Malvern instruments Ltd., UK). The analyses was performed at 25 °C with a 633 nm laser source. ZnO-NPs were suspended in Milli-Q water and to break apart the agglomerate of ZnO, stock suspension was probe sonicated at 30 W for 10 min.

2.3.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the specimens were recorded on a diffractometer (Siemens D5000 X-ray, Germany) by using Cu K_α radiation (0.154056 nm) at 35 kV and 30 mA. Scattered radiation was detected at ambient temperature at a scan rate of 1° min^{-1} and a step size of 0.01°. The diffraction angle of 2θ ranged from 2 to 70°. D-spacing between the crystalline layers of nanoparticles (the lattice spacing or crystalline interplaner distance) was estimated using the Bragg diffraction equation:

$$d = \lambda/2 \sin \theta \tag{1}$$