Trends in Food Science & Technology 51 (2016) 41–48

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: http://www.journals.elsevier.com/trends-in-food-science-and-technology

Review

Study of physical and mechanical properties of polypropylene nanocomposites for food packaging application: Nano-clay modified with iron nanoparticles

Mohammad-Javad Khalaj [a], Hamidreza Ahmadi [b], Rasoul Lesankhosh [c], Gholamreza Khalaj [a], *

[a] *Young Researchers and Elites Club, Saveh Branch, Islamic Azad University, Saveh, Iran*
[b] *College of Technology and Engineering, Saveh Branch, Islamic Azad University, Saveh, Iran*
[c] *Baspar Pishrafteh Sharif Company, Tehran, Iran*

A R T I C L E I N F O

Article history:
Received 5 December 2015
Received in revised form
14 February 2016
Accepted 15 March 2016
Available online 16 March 2016

Keywords:
Food packaging
Polypropylene
Nanocomposite
Permeability
Nanoparticles
Clay

A B S T R A C T

Polypropylene (PP) nanocomposites were prepared via melt interaction of clay in a twin screw extruder. The evaluation of PP nanocomposites containing montmorillonite (OMMT) with or without iron nanoparticles modification was studied for food packaging applications. The nanocomposites were investigated by thermal, mechanical, morphological and gas barrier analyses. The X-ray diffraction patterns of all nanocomposites revealed an increment in d-spacing of the OMMT layers and proved the compatibility of neat PP and clay, along with the intercalation and partial exfoliation of the layers. Addition of nanoparticles had reverse effect on the intercalation and exfoliation of the clay to some extent. Transmitting optical and scanning electron microscopy revealed certain homogeneity with uniform distribution of OMMT and nano-particles in the PP matrix. According to the acquired thermal properties, a tendency for the melting temperatures increased with the clay concentration. Also, crystallization temperature and crystallinity decreased with the clay concentration; however, nanoparticles compensated the effect of clay. Despite of no significant change in the ultimate tensile strength and elongation properties were observed in nanocomposites, the yield strength presented a substantial enhancement and the rigidity as well. Melt flow index (MFI) examination revealed decreasing melt viscosity of nanocomposite through increasing OMMT and iron nanoparticles. Besides, OMMT showed a high capacity to improve oxygen and water vapor barrier properties of PP. The use of clay increased the mobility distance of the gas molecules, led to oxygen permeability of neat PP being reduced whereas nanoparticle acted as an active oxygen scavenger and was capable of intercepting and scavenging oxygen by undergoing a chemical reaction with. Migration test also showed no restrictions in the use of nanocomposite films in food packaging.

1. Introduction

PP is one of the most widely used thermoplastics in the world due to its combination of easy processability, good balance of mechanical properties and low cost (Karian, 2003). However, PP has certain shortcomings that limit its use in some applications. One of these limitations is its poor oxygen barrier that prevents the widespread use of this material in the packaging industry (Ray & Okamoto, 2003).

Nanotechnology might be used to overcome these limitations because polymer/nano-clay composites demonstrate improved oxygen barriers and thermal properties (Hussain, Hojjati, Okamoto, & Gorga, 2006; Paul & Robeson, 2008; Ray & Okamoto, 2003; Santos, Liberman, Oviedo, & Mauler, 2009). Several research groups have dedicated substantial efforts toward improving the properties of PP/OMMT nanocomposites (Furlan et al., 2011; Reddy, Sardashti, & Simon, 2010). However, due to the lack of polar groups in the PP chains, it is still a challenge to disperse nonpolar nanofiller, like OMMT, into a PP matrix. Various methods have been described for the preparation of PP/OMMT nanocomposites. Melt

---

* Corresponding author.
E-mail address: gh.khalaj@srbiau.ac.ir (G. Khalaj).

http://dx.doi.org/10.1016/j.tifs.2016.03.007
0924-2244/

compounding is so far the most cited in the literature due to the easy processability of PP and the use of conventional processing equipment (Kato, Usuki, Hasegawa, Okamoto, & Kawasumi, 2011; Spencer, Hunter, Knesek, & Paul, 2011). PP/OMMT nanocomposites at low loading level of nanofillers often show notable improvements in numerous properties, such as Young's modulus, gas permeability and thermal stability. Svoboda et al. (Svoboda, Zeng, Wang, Lee, & Tomasko, 2002) reported an increase of 30% on the modulus of PP nanocomposites containing 5 wt% OMMT. Polymer/OMMT nanocomposites present improved gas barrier properties because the clay imposes a restriction to the gas diffusion. Choi et al. (Choi, Cheigh, Lee, & Chung, 2011) quantified influence of OMMT dispersion on the mechanical, thermal, morphological, and gas barrier properties of PP/OMMT nanocomposites. The results revealed that the tensile strength was maximal for PP/clay nanocomposites with 10 wt% OMMT compared to neat PP. The X-ray diffraction patterns of the nanocomposites revealed an increase in d-spacing of the OOMMT layers indicating that the compatibility of neat PP and OOMMT was improved by the addition of Maleated polypropylene (MAPP), as well as, the intercalation and partial exfoliation of the OMMT layers (Choi et al., 2011). The use of OMMT increased the mobility distance of the gas molecules led to the oxygen permeability of neat PP reduced up to 55% (Choi et al., 2011).

Among the approaches available to improve the barrier properties, one of the most promising approaches is the addition of an active oxygen scavenger directly into the PP matrix (Galotto, Anfossi, & Guarda, 2009; Hannon, Kerry, Cruz-Romero, Morris, & Cummins, 2015; Kuorwel, Cran, Orbell, Buddhadasa, & Bigger, 2015; Reig, Lopez, Ramos, & Cloquell Ballester, 2014). An active oxygen scavenger is such a substance capable of intercepting and scavenging oxygen by undergoing a chemical reaction with as the oxygen permeates through the PP packaging wall (Atayev & Oner, 2014; Majeed et al., 2013). The most conventional approach has been the use of a metal-based scavenger such as iron (Bhat et al., 2012). However, within these systems, the finely powdered and activated metal enters the oxide state when exposed to the appropriate humidity condition and effectively bonding oxygen in the process. Metal-based scavengers can exist in several forms. The most common form is the sachet where the ground metal is packaged in a highly permeable pouch. Recently, these oxygen scavengers were incorporated into the polymeric wall of food packaging (Zehetmeyer et al., 2012). Other metal-based scavengers include labels, coatings and extrusion additives (Duncan, 2011; Pannirslvam, Genovese, Jollands, Bhattacharya, & Shanks, 2008).

Considering that a high number of studies have been carried out on PP/clay nanocomposite (Dal Castel, Pelegrini, Barbosa, Liberman, & Mauler, 2010; Garcia-Lopez, Picazo, Merino, & Pastor, 2003; Ristolainen et al., 2005; Santos, Liberman, Oviedo, & Mauler, 2008; Ton-That, Perrin-Sarazin, Cole, Bureau, & Denault, 2004), there is still lack of knowledge involving addition of iron nanoparticle in nanocomposites applied in food packaging. On this basis, the aim of this study is to elucidate the potential of PP/clay/iron-nanoparticle nanocomposites as packaging materials for the food industry and to determine their mechanical, thermal, morphological, and oxygen permeability characteristics.

2. Experimental

2.1. Materials

PP homopolymer with a melt flow index (MFI) of 3.5 g.(10 min)$^{-1}$ (230 °C/2.16 kg) and density of 0.905 g cm^{-3} (23 °C) was produced by Bandar Imam Petrochemical Company, Iran. The used nano-clay mineral was the OMMT Cloisite® 15A, group of smectites, organically modified with a salt of alkyl quaternary ammonium, from Southern Clay Products.

Maleated polypropylene (MAPP; CM-1120H, Mw: 124,200 g mol^{-1}, MI: 80 g.(10 min)$^{-1}$, MAH graft ratio: 0.5–1.0 wt%) used as compatibilizer was received from Karan Gin Company, Iran. Iron nanoparticle colloid was produced via underwater high-voltage electrical explosion of wire by a Nano Colloid maker (PNC, Model: 1 k) from Nano Engineering and Manufacturing Company (PNF Co.).

2.2. Preparation of the nanocomposites

Iron nanoparticles distributed in distilled water as metallic colloid. Nanoparticles must be separated by centrifuge or spray dryer in a controlled environment (non-oxidizing). Then, the nanoparticles of iron and dried powder of clay (at 100 °C preserved for 24 h) was physically mixed with the polymer granules. Then, the mixture processed in a twin extruder ($\Phi = 19$ mm, L/D = 40) (a co-rotating twin screw extruder SHJ 20, China).

The nanocomposites with different proportions of the PP, OMMT, nano–iron and MAPP compatibilizer were prepared by a 1-step blending and melt-compounding in a twin extruder under the following conditions of:

- Processing temperatures: 180–200 °C,
- The screw speeds: 100–160 rpm, and
- The prepared pellets were dried at 90 °C for 24 h in a vacuum oven to remove the absorbed water prior to manufacturing the films that are used for oxygen permeability.

Table 1 summarizes the formulation of nanocomposites fabricated in this study. The neat block PP was used as a reference material.

2.3. Characterization of the nanocomposites

The mechanical properties of the materials were determined by tension test (ASTM D638). The tensile specimens were injection-molded and tension tests were measured using a universal testing machine equipped with Hounsfield 10K extensometer. The tensile strength was determined at crosshead speed of 10 mm min^{-1}.

The melting temperature, melting enthalpy, crystallization temperature, crystallinity enthalpy, and crystallinity percentage of the nanocomposites were measured using a differential scanning calorimeter (DSC; TA Q100 MDSC). The nanocomposites were first heated from 30 to 220 °C. A typical sample weight was about 5–10 mg and the scan speed was set 10 °C min^{-1}. All operations were accomplished under the nitrogen atmosphere in order to prevent oxidation. The melting and crystallization behaviors were determined from the first heating scan. The melting temperature

Table 1
Fabricated nanocomposites with different PP, OMMT, and iron nanoparticles proportions.

Sample designation	Clay (wt%)	Iron nanoparticle (wt%)
N0[a]	–	–
N1	1	–
N2	2	–
N3	4	–
N4	2	0.05
N5	2	0.1
N6	2	0.2

[a] Neat PP.