Polymer Degradation and Stability 121 (2015) 137–148

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Influence of zeolite nanoparticles on photostability of ethylene vinyl alcohol copolymer (EVOH)

Ievgeniia Topolniak [a], [b], Jean-Luc Gardette [a], [b], Sandrine Therias [a], [b], *

[a] CNRS, UMR 6296, Institut de Chimie de Clermont-Ferrand, BP 80026, F-63171 Aubière, France
[b] Clermont Auvergne Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, France

ARTICLE INFO

Article history:
Received 8 June 2015
Received in revised form
24 August 2015
Accepted 25 August 2015
Available online 31 August 2015

Keywords:
EVOH
Photooxidation
Zeolite
Nanocomposites

ABSTRACT

New ethylene vinyl alcohol copolymer EVOH nanocomposites based on zeolite particles were processed by solution or melt-mixing to synthesise potential encapsulants for flexible organic solar cells (OSC). The photochemical behaviour of pristine EVOH copolymer and the influence of zeolite particles with different size and increasing nanoparticle loading were studied to evaluate the photostability of such packaging materials. Photooxidation of pristine EVOH films (with two different ethylene unit contents (27% or 44%) was performed under accelerated artificial conditions that allow for the proposal of a comprehensive mechanism of EVOH oxidation. The photochemical behaviour of EVOH/zeolite nanocomposites with different morphology and size of particles was compared, revealing a higher oxidation of the polymer in the presence of zeolite particles, which can be mainly attributed to iron impurities.

1. Introduction

Over the previous 20 years, polymer nanocomposites (PNCs), which are particle-filled polymers with at least one dimension of the dispersed particles in the nanometre range, have attracted much attention. It has been demonstrated that introducing inorganic nanoparticles (usually at low content up to 5 wt%) into a polymer matrix improves several properties of the material in comparison with the pristine polymer. Among these properties are heat resistance [1–4], thermal [5,6], mechanical [7], electrical [8] properties, and barrier properties, such as a decrease of oxygen [6] and water vapour [9] transition rates (abbreviated OTR and WVTR, respectively) for nanocomposites with low nanofiller content (approximately 3–5%). These enhanced performances are attributed to the unique morphology with large interfacial area of nanoparticles as the supramolecular organisation of the particles is important to reach the desired macroscopic properties.

It is known that organic solar cells (OSCs), especially the active layer and electrodes, are sensitive to trace quantities of oxygen and humidity, which jointly with light, can strongly decrease the performance and the life-time of the device [10]. One solution to overcome this problem is the use of encapsulation to prevent oxygen and moisture from reaching the fragile components of the cell. The development of encapsulation materials for the photovoltaic module protection with high barrier properties is then one of the challenges for OSC competitiveness in the market [11]. The barrier requirement range for OSCs encapsulation is of ~10^{-3} cm^3 m^{-2} day^{-1} and ~10^{-6} g m^{-2} day^{-1} for OTR and WVTR, respectively. Moreover, these materials have to be stable within the operating life of the cells.

Among the polymers commonly used as barrier materials for applications such as food packaging, ethylene–vinyl alcohol copolymers (EVOH) have good barrier properties to oxygen ($OTR = 0.05$ cc day^{-1} atm^{-1}) for EVOH with 32 wt% of ethylene part and thickness 10 microns [12], considerable chemical resistance and high transparency, which make them good candidates for encapsulation coatings. Poly (ethylene vinyl alcohol) copolymers (EVOH) are randomly formed semi-crystalline polymers with different ratio of ethylene and vinyl alcohol groups from 24 up to 55 wt% of ethylene part. With increasing ethylene content in the copolymer, the water barrier properties increase, whereas the oxygen gas barrier properties decrease [13]. This opposite effect provides an opportunity to tune the chemical composition of the polymer for the desired property. The oxygen barrier properties of EVOH are extremely sensitive to moisture, therefore EVOH should be used as a core layer in multilayer packaging structures [14,15].

In terms of permeability coefficients, even the best polymeric

---

* Corresponding author. Clermont Auvergne Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, UMR 6296, ICCF, BP 80026, F-63171 Aubiere, France.

E-mail address: sandrine.therias@univ-bpclermont.fr (S. Therias).

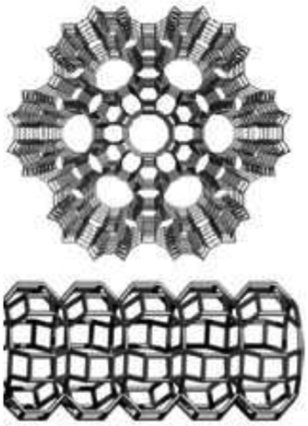
http://dx.doi.org/10.1016/j.polymdegradstab.2015.08.014
0141-3910/

barriers remain several orders of magnitude higher than the OPV requirements. Improving the barrier properties of the polymer is thus required, which could be achieved through the incorporation of inorganic particles into the polymer. The resulting increase of the barrier effect caused by the introduction of such passive particles is well known. This increase is majorly attributed to a lengthening of the permeation path due to the tortuous path [16] provoked by the particles; passive particles usually do not interact with the permeating gases either through sorption or chemical processes. It has been shown that in the case of EVOH the barrier properties can be increased by adding various types of nanofillers, such as organoclays (bentonite [17], kaolin [13], kaolinite [18], montmorillonite [9], layered double hydroxides [19]) or carbon nanotubes [20].

An alternative approach to the passive nanocomposite is the use of active fillers, which strongly interact with a permeating gas. These active fillers are commonly known as getters and their activity is to either consume a permeating gas through chemical reaction or to trap permeating gases via sorption processes. The common types of getters that can trap water through adsorption include molecular sieves such as zeolites. Zeolites are aluminosilicates, which have an ordered, highly porous structure that allows for a high water sorption capacity. As these getters need a high surface area to adsorb large quantities of gas, they are usually highly porous, often with pore diameters on the order of only a few nanometres. There exists a wide variety of zeolite structures, but zeolites are generally based on cage-like structures created by silicate and aluminosilicate tetrahedral (Scheme 1). These cages form a series of ordered pores with the smallest pore diameters in the range of 6–14 nm.

Of particular interest are zeolites as they have the ability to be manufactured as nanoparticles. Nanoparticles of zeolites have been well researched; however, their use in barrier composites has received only very limited attention [21,22]. For example, zeolites were proposed for use in electronics in 1990 [23] but were recently introduced into a device as a relatively thick non-transparent layer of particles in the bottom side of organic light-emitting device (OLED) [24] to ensure a dry environment.

It is worth considering that nanofillers can decrease the oxygen permeability of the polymer, which in turn could limit the oxidation rate of the polymer rate in the case of an oxygen diffusion controlled reaction. However, a drawback to the use of nanofillers is their negative impact on the photostability of the polymer. The addition of particles to polymers has been shown many times to affect the photostability of nanocomposites. Although inorganic particles rarely experience significant photodegradation under sunlight exposure, they can change the mechanisms and/or the rate of photooxidation of the polymer matrix and must therefore always be accounted for when determining the photostability of the nanocomposite. For example, some metal oxides such as zinc oxide and titanium oxide, can have a photocatalytic effect [25]. Conversely, lamellar nanofillers such as clays are reported to have a prodegradant effect on the polymer photooxidation [26–28] due to the presence of transition metal ions such as iron [29–32] that can produce a catalytic decomposition of hydroperoxides.



Scheme 1. Zeolite structure.

In summary, one should pay attention to the fact that the observed rate of oxidation results in a balance between the two competing processes, O_2 barrier and photocatalytic effects, with the photocatalytic effect being highly dependent on the chemistry and purity of both the nanofillers and the polymer.

This study is part of a work devoted to the development of EVOH/nanocomposites based on inorganic fillers such as zeolites for potential encapsulation coating for OSC. The present paper focuses on two fronts: on one side, the photooxidation of EVOH copolymers was studied through identification of the photoproducts, both in the solid and the gas phases; and on the other side, the photochemical behaviour of the EVOH/zeolite nanocomposites was characterised depending on the particle size and the zeolite loading of the materials. This research aims to propose nanocomposite coatings for flexible solar cells taking into account the photostability of the barriers used for encapsulation.

2. Experimental part

2.1. Materials

Ethylene vinyl alcohol copolymers (EVOH) containing 27 wt% (EVOH27) and 44 wt% (EVOH44) ethylene, were supplied by Scientific Polymer Products, INC. Most of the results were obtained with EVOH44 as polymer, and the polymer was named EVOH.

Dimethylsulfoxide (DMSO) solvent of 99.9% purity was purchased from Sigma Aldrich Ltd (St. Louis, MO) and used without further purification.

Synthetic zeolites were kindly supplied by Clariant Produkte (Deutschland) GmbH with the trade names Lucidot NZL 40 LP3533 (NZL) and Lucidot DISC (DISC). Particle specifications provided by the supplier are displayed in Table 1.

The chemical composition of zeolite particles (NZL and DISC) was checked by elemental analysis (*Service central d'Analyse of the CNRS at Vernaison*) (Table 2.). According to the analysis, the zeolites have the following formula: $[K_9(H_2O)_{16}]$ $[Si_{27}Al_9O_{72}]$ with Si/Al ratio close to 3, which is typical for L-type zeolites. The results indicated the presence of iron impurities in both samples, and other elements were detected in trace amount (≥20 ppm).

2.2. Preparation of EVOH/zeolite nanocomposites and film processing

Nanocomposites were prepared by two different methods: either solution casting (method A) or melt-mixing using a twin screw extruder (method B).

2.2.1. Method A

The polymer was dissolved in DMSO at 190 g/l. At the same time, a solution of zeolite particles with concentration of 95 g/l was placed in an ultrasonic bath for 30 min and then treated by an ultrasonic processor (a Vibra-Cell VCX 130 PB) for 5 min at a frequency of 20 kHz and amplitude of 75%, immediately preceding the mixing with polymer solution. After sonication, aliquots of zeolite suspension were added to achieve nanocomposites with 10, 20 and 30 wt% of particles to the fixed volume of EVOH solution. The