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J. M. Lagarón^{ab}; L. Cabedo^c; D. Cava^a; J. L. Feijoo^d; R. Gavara^a; E. Gimenez^{bc}

^a Packaging Lab, IATA, CSIC, Apdo. Correos 73, Burjassot E-46100, Spain ^b NanoBioMatters S.L., CEEI, Technological Park of Valencia, E-46980 Paterna, Spain ^c Department of Technology, University Jaume I, e-12071 caslon, Spain ^d Departamento Ciencia de los Materiales, Universidad Simon Bolivar, Caracas 89000, Venezuela

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Improving packaged food quality and safety. Part 2: Nanocomposites

J. M. LAGARÓN^{1,4}, L. CABEDO², D. CAVA¹, J. L. FEIJOO³, R. GAVARA¹,
& E. GIMENEZ^{2,4}

¹Packaging Lab, IATA, CSIC, Apdo. Correos 73, Burjassot E-46100, Spain, ²Department of Technology, University Jaume I, E-12071 Castellon, Spain, ³Departamento Ciencia de los Materiales, Universidad Simon Bolivar, Caracas 89000, Venezuela, and ⁴NanoBioMatters S.L., CEEI, Technological Park of Valencia, E-46980 Paterna, Spain

Abstract

This paper gathers a number of significant results where nanotechnology was satisfactorily applied to improve packaged food quality and safety by increasing the barrier properties to oxygen of an ethylene-vinyl alcohol copolymer (EVOH) in dry and under humid conditions and of a poly(lactic acid) (PLA) biopolymer. The nanodispersion in the polymer matrix of modified monolayers of clays included in positive lists for food-contact applications is an adequate methodology to increase packaged food shelf-life. In spite of the fact that, in principle, there is no reason to believe that 'adequately' modified nanocomposites making use of substances in positive lists can impose any immediate risk threat for food-contact applications, further studies concerning potential migration issues and life-cycle analysis have to still emerge within the overall field of nanotechnology to corroborate the fact.

Keywords: *Nanocomposites, permeability, EVOH, biopolymers*

Introduction

Packaging has developed into an essential technology in the handling and commercialization of food-stuffs to provide, by maintaining or even increasing, the required levels of quality and safety. However, as polymers have become more extended in food packaging applications over the last decades, many concerns have arisen over their characteristic ability to allow low molecular weight mass transport phenomena. Consequently, a great deal of research has been put forward to minimize these processes for the packaging of, for instance, oxygen-sensitive foodstuffs and, therefore, to guarantee food quality and also safety during the extended shelf-life of these products (Lagarón et al. 2004a). One of the most promising routes to accomplish this is through the development of 'ultra-high' barrier materials by means of nanotechnology.

Nanotechnology is by definition the creation and utilization of structures with at least one dimension in the nanometer length scale that creates novel properties and phenomena otherwise not displayed by either isolated molecules or bulk materials.

The recent discovery of organized structures such as totally exfoliated clay tactoids, nanofabrication of fibres, carbon nanotubes, molecular motors, DNA-based assemblies, quantum dots, molecular switches, surface engineering and self-assembly, and new intrinsic nanoscale phenomena (size confinement, magnetoresistance and the predominance of interfacial phenomena) offers great opportunities in many industrial applications. The interest in being capable of controlling size in the nanometer range lays on the fact that variations at the nanometer scale affect electronic and atomic interactions, hence allowing the controlled production of materials with varied properties without changes in chemistry. Finally, nanoscale structures display a high surface-to-volume ratio, which is ideal for applications that involve composite materials, chemical reactions, drug delivery, controlled and immediate release of substances in active and functional packaging technologies, and energy storage, for instance in intelligent packaging (Shonaike and Advani 2003).

Among the various existing nanotechnologies available, the one that has attracted more attention

in the packaging field is the nanocomposites. Nanocomposites are a relatively new family of composite materials in which at least one of the dimensions of the filler is in the nanometer range. It has been broadly reported in the literature that the addition of low loadings of nanoparticles to a raw polymer can have a profound enhancing effect over some material properties, such as mechanical properties, thermal stability (Kotsilkova et al. 2001), conductivity and gas barrier properties, without significant reduction in other relevant properties including toughness (Alexandre and Dubois 2000) and, as long as the clay content is below a critical loading level, transparency (Wan et al. 2003).

Among the nanocomposites, the most commonly studied materials are the clay/polymer nanocomposites. The clay generally used in these materials is a commercial modified montmorillonite (MMT), which has already shown improvements in the gas barrier and mechanical properties of, for instance, ethylene-vinyl alcohol copolymers (EVOH) (Cabedo et al. 2004; Lagarón et al. 2004b). The long aspect ratio of the clay nanolayers and their impermeability results in increased tortuosity factors and, therefore, in delays in the diffusion of penetrants through packaging materials and structures. In this work, however, a different clay, i.e. natural kaolinite, has been used. The kaolinite is a very common material in earth, very cheap and, hence, widely used as raw material in many industrial sectors. The kaolinite used here is generated as a recyclable residue in the local tile industry (its small agglomerate size and low content of crystalline silicon oxide makes it unsuitable for the production of tiles). Therefore, the price of this material residue is very low and far more inexpensive than the conventional commercial montmorillonite and, thus, shows great potential as an affordable high 'added value' nanotechnology element for the food packaging industry.

In this work, the potential of nanocomposites to improve barrier properties in food packaging applications will be shown and discussed.

Materials and methods

Materials

The proprietary modified clays were supplied either as powder or masterbatch (case of EVOH, 25% of clay) by (www.nanobiomatters.com) NanoBioMatters S.L., Spain. Before chemical modification, the raw clay from the tile industry (P.O. 161 Alcora, Spain, Arciblansa S.L., Spain) was first screened through a 40- μm sieve to remove crystalline silicon oxide, iron and iron oxide impurities. To enhance the dispersion of the aggregates, it was first introduced in an ultrasound field for

10 min, the sieved suspension dried at 100°C and milled; it was then subjected to appropriate chemical modification with substances present in positive lists for food contact, not disclosed by the manufacturer. A commercial montmorillonite clay modified with alkyl ammonium salts was supplied by Laviosa Mineraria, Italy (www.laviosa.it).

Nanocomposite specimens of EVOH and aPLA with 5 and 4% clay loadings, respectively, were obtained by melt blending in an internal mixer (Rheomix-Haake) during a mixing time of 10 min above the melting point of the polymer and with a rotor speed of 100 rpm. The ethylene-vinyl alcohol copolymer (EVOH) used was a commercial product (Soarnol[®]), containing 32 mol% ethylene, kindly supplied by The Nippon Synthetic Chemical Industry Co. Ltd. (NIPPON GOHSEI; Osaka, Japan (www.nichigo.co.jp/english)). EVOH pellets were vacuum dried at 90°C during 48 h and for 1 h at 110°C immediately before the blending step. Amorphous poly(lactic acid) (aPLA) containing 12 mol% D-lactide was supplied by (www.lactic.com) Galactic (Belgium). The nanocomposites resulting from the mixing were cooled with liquid nitrogen and ground into powder in a rotating mill. The nanocomposite powder was manually cleaned under magnification lens to remove residues. Polymer sheets (0.8 mm thick) and films (120 μm thick) were obtained by compression moulding from the melt and allowed to cool at 20°C min⁻¹ to room temperature under pressure. The films and plates were used to measure oxygen permeability.

Techniques

TEM observations were carried out in ultrathin-sectioned samples (below 100 nm). The specimens were cut using a microtome (Ultracut E) equipped with a diamond knife. The TEM micrographs were obtained with a JEOL 1010 provided with a digitalization system of images Bioscan (Gatan). Scanning electron microscopy (SEM) observations were carried out with a Jeol JMS-6300. Samples were cryofractured and gold coated before SEM observations.

The oxygen transmission rate through compression moulded film specimens of EVOH nanocomposites was measured at 21°C using an Oxtran 2/20 instrument (Modern Control, Inc., Minneapolis, MN, USA). The detection limit of the instrument was of 10⁻²¹ m³ m m⁻² s Pa. The measurements at high relative humidities (RH), i.e. 85% RH and 94% RH, were carried out by preconditioning the specimens at the desired RH in salt solutions until constant weight. The samples were then immediately wax coated to diminish the loss of moisture and immediately tested for

their oxygen permeability. This method proved to be very efficient in determining oxygen data at high RH because permeabilities for pure EVOH were in good agreement with previously reported results (Aucejo et al. 2000). Data at lower RH could not be measured because the nanocomposite was below the limit of detection of the instrument. Dry specimens were attempted at 45°C, maximum temperature that the instrument allows, and even at this high temperature only the EVOH sample could be measured, $4 \times 10^{-21} \text{ m}^3 \text{ m}^{-2} \text{ s Pa}$, being the nanocomposite always below the limit of detection of the instrument.

aPLA nanocomposites were measured at 21°C and 40°C RH in an Oxtran 100 (Modern Control) through 0.8-mm-thick plates.

The transport properties of water were measured by both weight loss experiments using Davenport caps (UK) sealed with wax, and through water weight gain experiments.

Results and discussion

Figure 1 shows SEM and TEM pictures of EVOH/kaolinite nanocomposites. They clearly indicate that there is a large fractionation of the clay agglomerates. From the SEM picture, a strong adhesion between clay and polymer matrix can be inferred. Dispersion and fractionation of the clay is inferred from the TEM picture. This picture clearly suggests that there is some degree of exfoliation in the structure of the polymer but that this is not total, since intercalated tactoids (not totally exfoliated agglomerates) are still observed.

Nevertheless, these intercalated morphologies still provide relatively high averaged aspect ratios ($L/2W$) of around 40, where L is platelet length and W is platelet thickness.

Regarding barrier properties, it is reckoned that the presence of exfoliated layers of clay in the polymer results in enhancement of the so-called tortuosity (or detour) factor (Lagarón et al. 2004a). Equation 1 shows the simplest equation for modelling permeability of systems comprising impermeable plates of a filler-oriented perpendicular to the permeant transport direction and evenly dispersed across the polymer matrix:

$$\frac{P_{\text{nanoblend}}}{P_{\text{pure}}} = \frac{1 - V_{\text{clay fraction}}}{1 + (L/2W) \cdot V_{\text{clay fraction}}} \quad (1)$$

Therefore, the higher the aspect ratio ($L/2W$) and the volume fraction of clay, the higher the expected barrier improvement in the nanocomposite. Figure 2 shows oxygen permeability and water vapour transmission rates of neat EVOH and EVOH nanocomposite. It clearly suggests that the permeability of the polymer is significantly improved (for oxygen permeabilities, see Table I) at high RH and also under dry conditions. Dry oxygen permeability was measured at 45°C in the sample to enhance transmission rate in an attempt to surpass the detection limit of the permeability kit. Even under these circumstances, the permeability of the EVOH nanocomposite could not be measured (Cabedo et al. 2004). These results are of significant relevance in food and beverage packaging sectors because prove that nanocomposites can be used to increase shelf-life of products

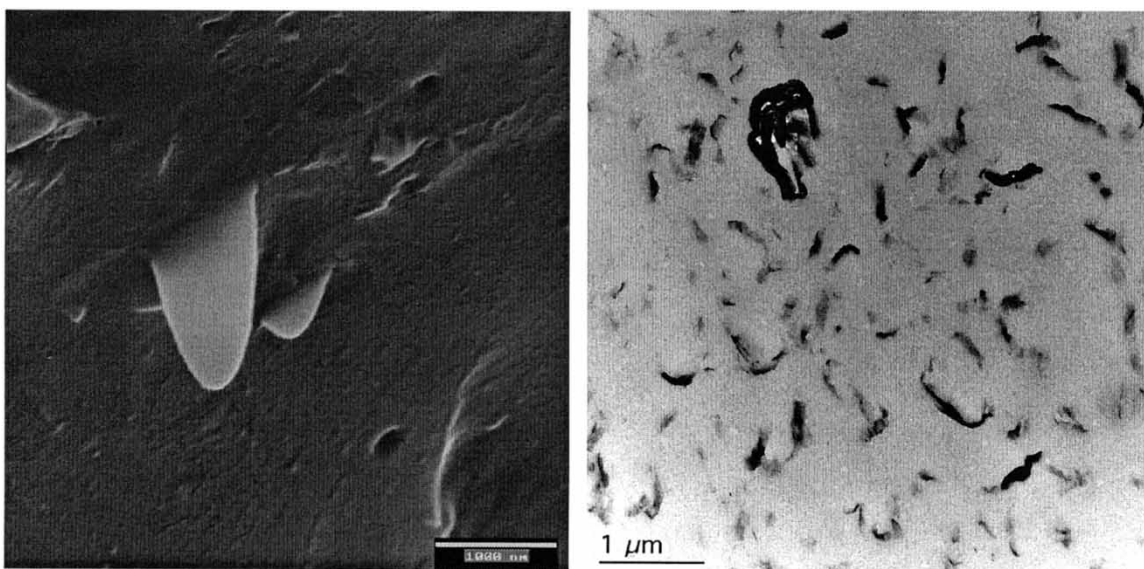


Figure 1. SEM (left) and TEM (right) micrographs of EVOH nanocomposites.

packaged in commodity plastics; and/or to transform high-barrier materials into virtually impermeable materials with decreased water sensitivity in barrier.

Figure 2 also shows water weight loss permeation experiments for neat EVOH and nanocomposite. Surprisingly, the barrier to water of the nanocomposite is similar or slightly higher than that of the pure EVOH. From the results, it is remarkable to observe that the strong adhesion between clay and polymer does not allow an increase in the transport rate of water through the nanocomposite, even when the clay has a strong affinity for moisture. This observation can thus help explain the improved

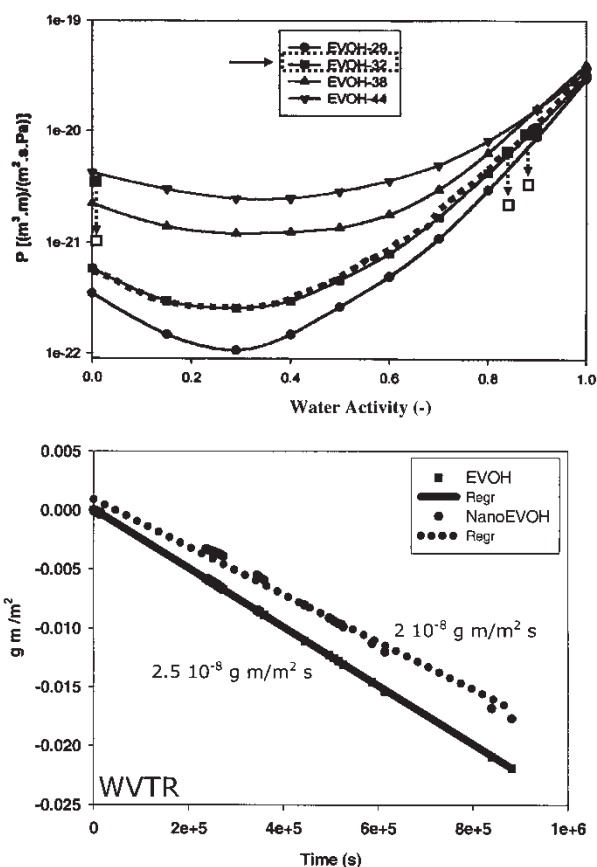


Figure 2. Oxygen permeability (top) of EVOH as a function of ethylene content and relative humidity at 21°C. Filled squares are permeability data for pure EVOH32; open squares are data for EVOH32 nanocomposites. The data at 0% RH for EVOH32 were carried out at 45°C. Water vapour transmission rate (bottom) for EVOH32 and nanocomposite.

oxygen permeability of the nanocomposite at high RH.

Figure 3 shows that the clay can also be dispersed very finely through the matrix of a biopolymer, aPLA. Nevertheless, no full exfoliation was observed as some clay agglomerates can still be seen spread across the polymer matrix.

Figure 4 shows the oxygen permeability for this polymer and nanocomposites and for other reference materials. From the results, it is clear that the barrier properties to oxygen in both nanocomposites are improved. However, the barrier improvement is clearly smaller compared with that measured in EVOH. This suggests that optimization of the nanocomposite for the aPLA matrix is still needed, and that one modification of kaolinite or even the most typical commercial modification for montmorillonite cannot be generally applied to all materials and yield optimum performance.

Figure 5 shows water uptake results as a function of time. It is clear that the sorption of water does not follow a Fickian behaviour and this is higher for the nanocomposites, albeit the diffusion is slightly slower. The sorption of this component, however, does definitely affect the polymer stability as the polymer swells continuously over time.

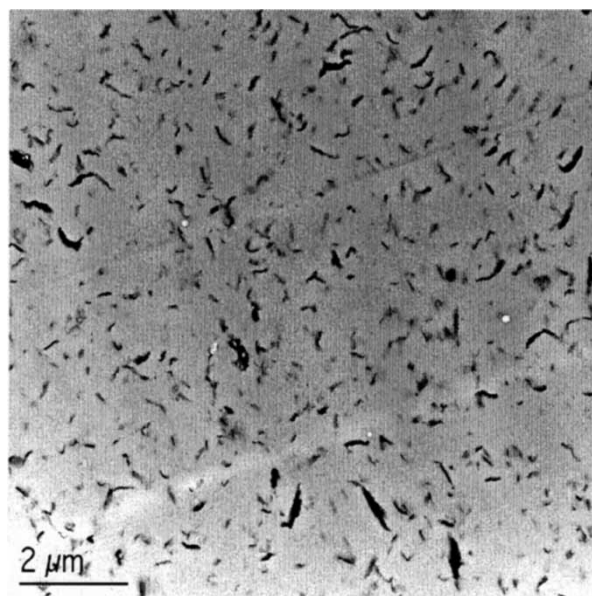


Figure 3. TEM micrograph of the aPLA-kaolinite nanocomposite.

Table I. Oxygen permeability ($\text{m}^3 \text{m m}^{-2} \text{s Pa}$) of EVOH, aPLA and nanocomposites.

| Sample | EVOH | NanoEVOH | aPLA | Nano(aPLA)-K | Nano(aPLA)-MMT |
|--------------|---------------------|---------------------------|----------------------|---------------------|----------------------|
| 48°C, 0% RH | 4×10^{-21} | Below 1×10^{-21} | — | — | — |
| 21°C, 94% RH | 9×10^{-21} | 3×10^{-21} | — | — | — |
| 21°C, 85% RH | 7×10^{-21} | 2×10^{-21} | — | — | — |
| 21°C, 40% RH | — | — | 11×10^{-19} | 6×10^{-19} | 10×10^{-19} |

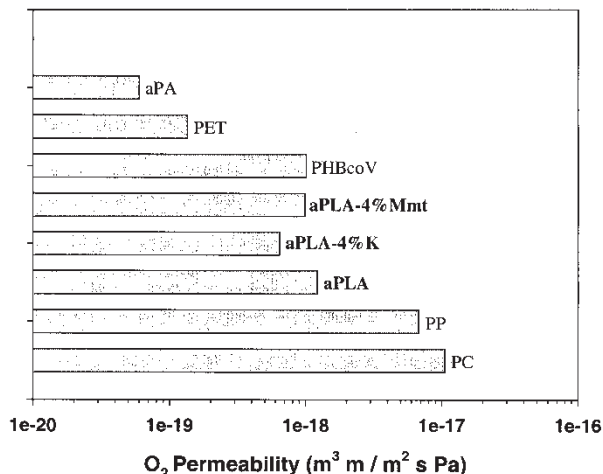


Figure 4. Oxygen permeability of pure aPLA and nanocomposite, amorphous polyamide (aPA), polyethylene terephthalate (PET),

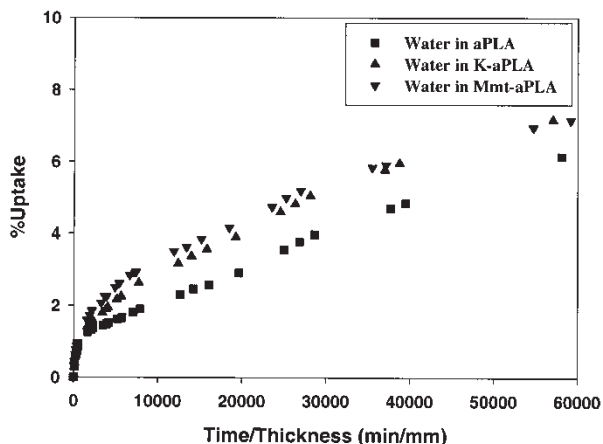


Figure 5. Water uptake (%) as a function of time for aPLA and nanocomposites.

Higher sorption of solvents and slower kinetics could make nanocomposites also suitable for controlled release of substances, for instance in active packaging technologies. Some work is being carried out in our group to tailor this behaviour in antimicrobial packaging applications.

Conclusions

From the results, it is clear that there is a huge potential in the nanocomposites field to enhance

the quality and safety of packaged foods by increasing the barrier properties of the packaging materials with low additions of highly dispersed nanoclay additives. There is, however, a need for a solid understanding and modelling of the relation between optimum barrier properties and characteristics such as clay modification, dispersion and adhesion for each polymer matrix. Finally, there is also an urgent need to regulate the use of these materials and especially caution should be taken regarding the use of potentially toxic chemical modifications of the clays for food-contact applications.

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