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Effect of food additives on the microstructure, mechanical and water transport properties of polyurethane films

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ABSTRACT

The objective of this work is to study the effects of common food preservatives (BHT, α-tocopherol, EDTA-Na and potassium sorbate) on the morphological, mechanical and water transport properties of polyurethane (PU) as films or coatings. The influence of these additives on the polymer structure and the polymer-additive interaction was evaluated by using SAXS, FTIR and DSC. The addition of additives results either in the formation of aggregates or modification of the polymer microstructure, depending on the molecular size and nature of additive, i.e. number of polar groups, hydrophilicity, etc. The addition of BHT molecules seems to break the typical hard segments interactions in PUs, leading therefore to a good incorporation of the molecule in the polymer matrix, however, α-tocopherol does not incorporate onto the PU matrix leading to an evident phase separation and not affecting therefore the microrange of heterogeneities of the PU matrix. On the contrary, films doped with EDTA-Na or potassium sorbate showed important changes in both soft and hard segments domains. As consequence, the water transport properties were greatly affected by the incorporation of these food additives in the polymeric matrix. Films with potential antimicrobial or antioxidant activity were obtained, with a moderated decrease in the mechanical properties.

1. Introduction

The incorporation of an active compound to a polymeric matrix can provide distinctive functionalities and in particular as controlled release system. The effects of the incorporation of additives on the morphological structure of a polymeric coating is an important aspect in film characteristics from a practical point of view, due to changes for example in the rate of permeation of molecules through the film, or film mechanical properties, as well as other surface and bulk properties.

Polyurethanes are one of the most popular film-based materials and they have attracted considerable attention since they combine a variety of functional groups into a single material, which have the possibility of tailoring their properties by varying the polymer composition. These polymers are composed of alternating urethane and polyol segments, formed in the reaction of organic diisocyanates with high molecular weight polyols, and optionally with low molecular weight chain extenders [1]. Micro and/or nanophase separation in this type of materials due to thermodynamic incompatibility between segments with different characteristics is often observed, which leads to organization of hard-segment (HS) domains dispersed in the soft-segment (SS) matrix [2,3]. The microstructure of this microphase separation was assumed to be lamellar [2], but now it is considered to be rather unknown [3].

The addition of an active compound to this polymeric matrix would produce microscopic and also macroscopic changes in the coating structure. If the relevant structural features are at a superatomic level, from 1 to 100 nm, small-angle X-ray scattering (SAXS) is the most broadly used technique for studying them and particularly for PU films morphology. The morphological properties of polyurethane-based polymers were studied extensively by SAXS by Muszynski et al. [1] and Desper et al. [3] among others.

On these changes, as well as on the action of the active compound, will depend the properties and applicability of the final

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material. In this sense, solute and solvent transport properties probably are one of the most affected by the addition of and additive to a polymeric matrix.

For non-porous materials there are no theoretical differences between the permeation of liquid water and water vapor [4]. The water molecules are transported through activated diffusion in both liquid and gas state. According with the ¨free volumë theory, the diffusion of the penetrant takes place through ¨holeš that are formed as a result of polymer chains motions. Water molecules may congregate in discrete clusters at polar sites and in free volume locations within some polymer films of intermediate polarity under high humidity or immersion conditions. A softening of the film due to plasticization could occur at the same time during this clustering. The plasticization or free volume expansion of the film is caused by separation of chains by the ¨propping opeñ action of the clusters between adjacent chains [5].

Swelling is defined as the increase of volume of a material (in this case a polymer film), due to absorption of a defined solvent. At first, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer–polymer intermolecular forces (crosslinking, crystallinity, or hydrogen bonding) are high enough, this is all what happens. But, if these forces are overcome by the introduction of strong polymer–solvent interactions, a second stage, the dissolution of the polymer, can take place [6].

The objective of this paper is to study the effects of some common food additives on the morphological structure and transport properties of PU films. In this way, compounds of recognized preservative action (BHT, Toc, EDTA-Na and KS) were incorporated at different concentrations to a polyurethane matrix. The influence of these additives on the polymer structure and the polymer-additive interaction were evaluated by using SAXS, FTIR and DSC. Mechanical, water swelling and water vapor permeability properties were also studied.

2. Experimental

2.1. Reagents

Isophoronediisocyanate (IPDI, Aldrich), dimethylol propionic acid (DMPA, Aldrich), 2-hydroxy ethylmethacrylate (HEMA, Aldrich), triethylamine (TEA, Anedra), potassium persulfate (KPS, Anedra), hydrazine monohydrate (HZN, Aldrich), dibutyltindilaurate (DBTDL, Aldrich) were of analytical grade and used as received. Polypropylene glycol 1000 (PPG1000, Voranol 2110) was dried and degassed at 80 °C at 1–2 mm Hg before used. α-Tocopherol (Toc, Parafarm), butylatedhydroxytoluene (BHT, Parafarm), Sorbic acid, potassium salt (KS, Anedra) and Etylendyamintetracetic acid, disodic salt (EDTA-Na, Anedra) were of food grade and used as received.

2.2. Polymer dispersions synthesis

Polyurethane (PU) was synthesized following a prepolymer mixing process, by polyaddition of IPDI, PPG1000, HEMA and DMPA. The PU anionomer having 2-ethoxymethacrylate terminal groups was dispersed in water prior neutralization of carboxylic acid groups with TEA and chain extended with HZN in water. A dispersion polymerization of the polyurethane aqueous dispersion containing double bonds was performed using KPS as initiator and leading to the formation of a crosslinked polyurethane. The resulting product was a stable dispersion with solid content of about 30 wt.%.

More experimental details on synthesis and characterization can be found in previous papers [7,8].

2.3. Incorporation of the additives

Incorporation of different amount of the additives to the polymeric matrix was made from their dissolution in the minimum quantity of acetone (Toc and BHT; 1, 2 and 5 wt.%) or water (KS and EDTA-Na; 0.5, 1 and 2 wt.%), and the addition drop by drop of this solution to the polymer dispersion under magnetic stirring at room temperature for five minutes. The amount of active compound in the film is expressed as wt.% on based on dried polymer.

2.4. Film formation

Sample films of PU and doped PU were prepared by casting the dispersions on a Teflon plate and evaporating the water and acetone at room temperature in the darkness; this process takes about 24 h. Then, formed films were cured at 60 °C for 48 h.

2.5. Fourier transformed infrared (FTIR) spectra

The FTIR spectra of additives, PU and additive-doped films were measured in the transmission mode or ATR, using a FTIR Nicolet 380 spectrometer and the corresponding ATR accessory. Sample films were prepared as in Section 2.4 and pure additives spectra were run using KBr in transmission mode. The number of scan per experiment was 64, with a resolution of 4 cm^{-1}.

2.6. Small angle X-ray scattering (SAXS)

SAXS measurements of films samples were performed at the SAXS2 beam line at the Synchrotron Light National Laboratory (LNLS) at Campinas (Brazil). A monochromatic beam of wavelength 1.608 Å was used and the exposure time was 300 s. The scattering intensity was registered using a bi-dimensional detector using a sample–detector distance of 728.32 mm for values of scattering vector $0.02 < q < 0.34\,\acute{\text{Å}}^{-1}$ ($q = (4\pi/\lambda)\sin(\theta/2)$; θ: scattering angle; λ: wavelength). One-dimensional curves were obtained by integrating the two-dimensional data with the program FIT2D. The acquired data were corrected by subtracting the background contribution of the empty cell.

2.7. Differential scanning calorimetry (DSC)

DSC was performed with a Shimadzu (Kyoto, Japan) DSC-60 instrument between −100 and 270 °C at a heating rate of 10 $^\circ\text{C min}^{-1}$. The samples were first heated to 150 °C at 30 $^\circ\text{C min}^{-1}$ and then cooled down at 30 $^\circ\text{C min}^{-1}$ before scanning to erase their thermal history. A nitrogen gas purge (50 ml/min) was applied, and the second heating curves were used for analysis.

2.8. Scanning electron microscopy (SEM)

The morphology of the surface and the cross-section of the film were observed with a scanning electron microscope Jeol JSM-6460. The samples were immersed in liquid nitrogen to fracture and then were sputtered with an Au-Pd mixture.

2.9. Mechanical properties

Tensile properties (such as tensile strength, elongation at brake and tension at brake) of the polymer films were measured at 25 °C using an EMIC DL-3000 (EMIC Ltda., San Pablo, Brazil) tensile-testing machine. Dog-bone-type specimens of 0.250 mm thickness, 6 mm width and 33 mm length were prepared, according to the test procedure given in ASTM D-638 (type IV specimen), and a testing speed of 500 mm min^{-1} was used.