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

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## ARTICLE INFO

## 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.

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## 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 super-atomic 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 volume¨ theory, the diffusion of the penetrant takes place through ¨holes¨ 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 open¨ 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 $80\,^{\circ}$C at 1–2 mm Hg before used. $\alpha$-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 $60\,^{\circ}$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 $0.02 < q < 0.34\,\text{Å}^{-1}$ ($q = (4\pi/\lambda)\sin(\theta/2)$; $\theta$: scattering angle; $\lambda$: 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 $270\,^{\circ}$C at a heating rate of $10\,^{\circ}$C min$^{-1}$. The samples were first heated to $150\,^{\circ}$C at $30\,^{\circ}$C min$^{-1}$ and then cooled down at $30\,^{\circ}$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 $25\,^{\circ}$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.

## 2.10. Water vapor permeability

The Water Vapor Permeability (WVP) test was conducted gravimetrically using ASTM procedure E96-95 (1995). At first, the measurement cells filled with anhydrous calcium chloride desiccant to create a 0% RH storage condition and the surfaces of cells (18.85 cm$^2$) were covered with the films and sealed with molten paraffin. To maintain a 75% RH gradient across the film at 25 °C, a sodium chloride-saturated solution was used in the desiccator. The RH difference between two sides of the films creates a vapor pressure equal to 1753.55 Pa. Once steady state was reached, the cells were weighted at 1 day intervals during 5 days by a digital balance (GK1203, Sartorius Co., Germany) nearest to the 0.001 g. The slope of the weight gain (g) versus time (h) was obtained by linear regression. Water vapor permeability was calculated by the following equation: WVP = (Curve slope × Thickness)/(Area × Pressure difference).

## 2.11. Degree of swelling

The measurements of water-swelling degree were performed using circular films, (25 mm diameter and 0.250 mm thickness), by the immersion/gain method. Firstly, the original weight of film was recorder with an accuracy of 0.001 g. Then, the film was immersed in an excess amount of distilled water. Wet samples were blotted between filter papers to remove the excess of surface liquid and reweighed periodically. The degree of swelling was measured in terms of the amount of absorbed water, using equation (1):

$$DS\% = \left(\frac{W_w \; W_i}{W_i}\right) \times 100 \qquad (1)$$

where $W_w$ and $W_i$ are the weights of the wet and initial (dried) samples respectively. The assays were performed at room temperature for triplicate.

## 3. Results and discussion

### 3.1. Small angle X-ray scattering (SAXS)

Analysis of the SAXS profiles of the initial PU matrix (Fig. 1) showed the existence of a single broad interference maximum at q = 0.1 Å$^{-1}$, which indicate the presence of periodicity in the spatial distribution of microranges of heterogeneity differing by the value of the local electronic density. This reveals low level of the scattering intensity in the interval of q from 0.02 to 0.34 Å$^{-1}$, indicating a low degree of the microphase separation of the rigid (HS) and the flexible (SS) blocks. The relatively good mixing of the blocks is mainly a result of the low fraction of the rigid blocks in the polyurethane prepared in this work (20.5 wt.%), of the asymmetrical structure of the diisocyanate fragments, and the PPG polyol for making the flexible blocks [2,9,10].

Therefore the PU prepared in this work is a polymer with weakly expressed microphase structure. As this PU is amorphous, the microranges of heterogeneity can be both the associations of the rigid blocks, that are fragments of diisocyanate with urethane groups in the chain, and the microranges enriched with the flexible blocks [2]. The interdomain repeat distance, d, between the microphases was determined from equation d = 2π/q* (where q* is the q value for the maximum). For pure PU the value founded about 63 Å ($q^* = 0.1$ Å$^{-1}$) is in coincidence with the reported ones in different PU systems [11–14]. Incorporation of different additives in the IPDI-based polyurethane has an influence on the microphase behavior of the final polymer material by altering the interaction between chains and therefore the shape and size of polyurethanes domains.

In BHT doped films (Fig. 1a), a decrease of the intensity of the typical peak at 0.1 Å$^{-1}$ was observed for all concentrations, but the remainder part of the spectrum was unchanged. In Toc doped samples (Fig. 1b) a different behavior was observed. With increasing additive content from 1 to 5 wt.%, the SAXS intensity was different than the corresponding to pure PU. The signal centered at
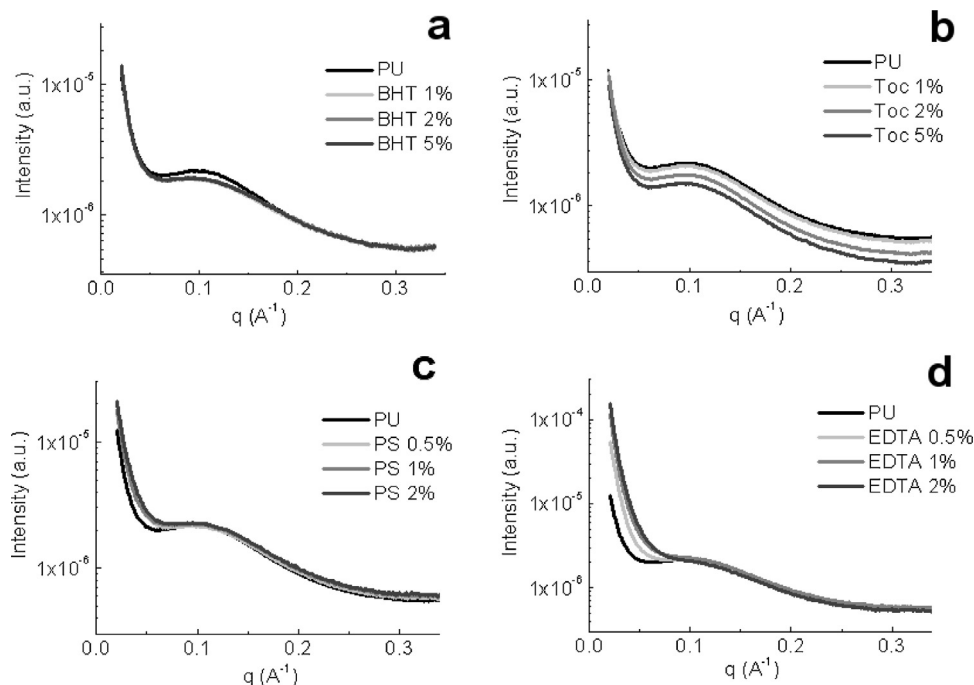


**Fig. 1.** SAXS spectrums of pure and active films; a) BHT, b) Toc, c) KS, d) EDTA.
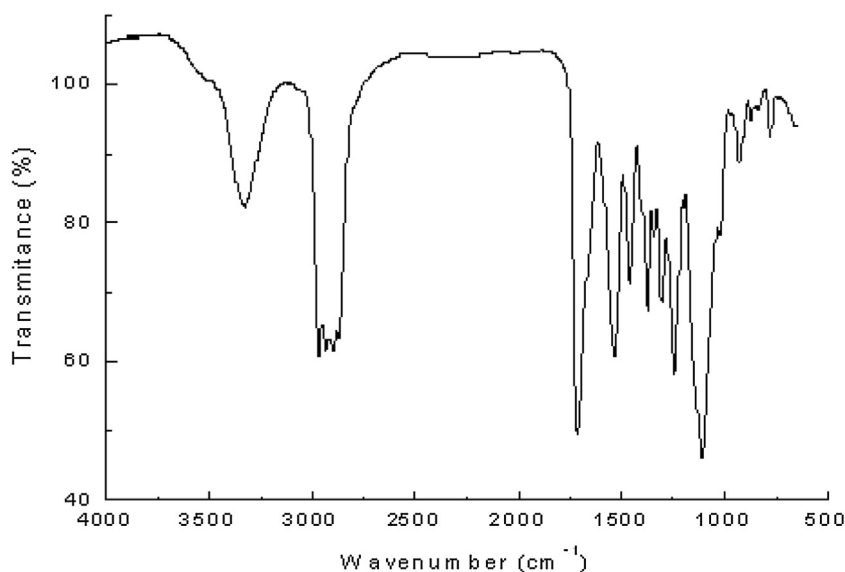
**Fig. 2.** FT-IR spectrum of PU film.

0.1 remained unchanged because this substance did not affect the microrange of heterogeneity in the PU matrix.

Differences in sizes between BHT and Toc might account for the differences observed in the SAXS spectra of the corresponding films. Although BHT and Toc are both hydrophobic substances, Toc, with a longer aliphatic chain, is a bigger molecule than BHT and may result in a poor compatibility in the polymeric film and therefore a limited incorporation of the additive in the PU matrix (see SEM results below). In the case of the BHT, it is dispersed in the matrix regularly with a probable preference for flexible blocks, due to its medium polarity and the relatively small size of the molecule, interacting through the hydroxyl group and forming hydrogen bonds with hydrogen acceptors in the polymer chains like the —O— groups in the polyether segments. However interaction with the carbonyl groups in the urethane moiety is also possible. The latter explains the decrease in the intensity of the peak observed at 0.1 $\text{Å}^{-1}$, due to the interaction of BHT with urethane linkages of polyurethane chains. This may affect the arrangement of these segments in the polymer film, producing materials with reduced phase separation, leading to loss of its typical SAXS signal.

SAXS spectra of films doped with EDTA-Na (Fig. 1c) and KS (Fig. 1d) showed an important change at q values around 0.08 $\text{Å}^{-1}$. An increasing scattering intensity, while increasing the additive content in the polymeric film, was observed and it was attributed to an increase of the electronic density difference between the different segments. Unlike BHT and Toc, EDTA-Na and KS are ionic compounds and specific ionic interactions preferentially with the urethane groups are expected and changing therefore the local electronic density and/or the interdomain distance, increasing the contribution at low q in SAXS spectra.

### 3.2. Fourier transformed infrared (FTIR) spectra

More insights on interactions in doped films were obtained from their FTIR spectra.

Fig. 2 shows the spectra of pure PU film. Typical bands at around 3332 $cm^{-1}$ and 3444 $cm^{-1}$ arising from H-bonded N—H and free N—H stretching vibrations, respectively, C=O bands (located between 1760 and 1610 $cm^{-1}$) corresponding to urethane groups, a signal centered at 1305 $cm^{-1}$ (combination of NH bending and C—N stretching), another absorption at 1239 $cm^{-1}$ (Amide IV band), and

a band at 1110 $cm^{-1}$ (C—O—C stretching vibration of polyetherdiol) [8] were observed.

Bands due to non-associated and associated C=O groups can be distinguished in the FTIR spectra of the PUs. The band due to non-associated C=O groups was located at 1716 $cm^{-1}$ (Fig. 3), whereas at 1670 $cm^{-1}$ there was another C=O band (shown as a shoulder in the main carbonyl band) due to hydrogen bonded urethane groups (associated carbonyl).

The maximum of this band was displaced slightly to lower wavenumbers as the BHT additive is incorporated in the PUs, indicating an interaction through H bonds between the carbonyl group of the polyurethane and the phenolic hydroxyl group of the BHT. This interaction was confirmed by the displacement of the band attributed to the phenolic hydroxyl group in the doped film (3627 $cm^{-1}$ in the pure additive and 3645 $cm^{-1}$ in the BHT added film).

The observed reduction of the intensity of SAXS peak is consistent with the proposed interaction and with the good incorporation of BHT in the polymer matrix.
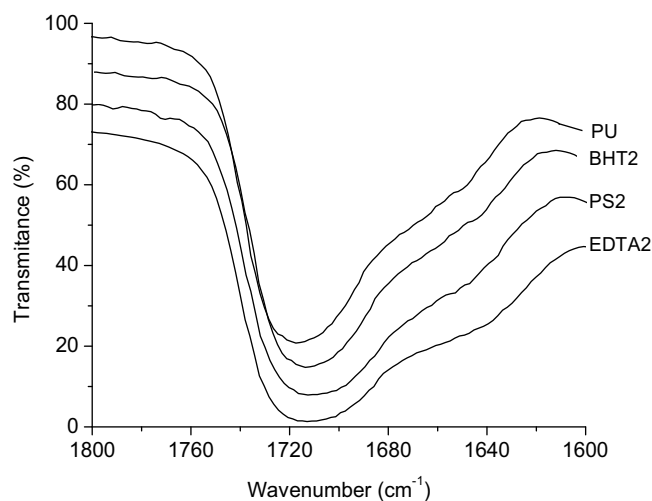


**Fig. 3.** FTIR spectra in the carbonyl region of pure PU and BHT, PS and EDTA 2 wt.% doped film.

α-Tocopherol doped films show a different behavior. Contributions from pure additive were observed at $2920\,cm^{-1}$ for the stretching modes of $CH_2$ and $CH_3$ residues, and 1758 and $1205\,cm^{-1}$ from the benzene ring deformation. A detailed analysis of FTIR spectra shows that the spectrum of Toc-doped PU film is similar to the addition of the pure components, indicating that no specific interactions between them are occurring. ATR spectra (see additional data) show accumulation of additive at the air-film interface as a result of segregation and migration. On the contrary, ATR experiments of BHT-doped films shown similar spectra of both air and substrate interface, indicating a homogeneous distribution inside the film as a consequence of specific (hydrogen bonds) interactions.

The FTIR spectra of KS and EDTA-Na doped films were expected to show more changes due to the ionic nature of these additives and therefore stronger interactions with the polymer matrix.

Fig. 3 shows the FTIR spectrum of 2 wt.% doped KS and EDTA films in the C=O stretching region. This band was observed at $1716\,cm^{-1}$ in the pure PU and shift slightly to lower wavenumbers ($1712\,cm^{-1}$) and becomes broader in KS samples, indicating that carbonyl groups are involved in the interaction with the molecules of the additive, probably through their carboxylic group. The NH stretching band is also affected by the incorporation of KS. The intensity of the $3520\,cm^{-1}$ band assigned to "free" NH was increased and the $3330\,cm^{-1}$ band (NH "bonded") shifted to lower wavenumbers and become broader when the additive is incorporated. These changes are attributed to the fact that the ionic additive incorporated to the PU matrix associate with the C=O groups throughout hydrogen bonds, breaking N—H···O=C interactions on the hard segments, and therefore generating "free" NH groups, but with no significant changes in the quantity of both free and bonded C=O groups.

The FTIR spectra of EDTA-doped films showed additional and shifted bands compared to pure PU at $2951\,cm^{-1}$ (OH stretching); 1713, 1640, 1530 (carboxylic groups vibrations) and $1300\,cm^{-1}$ (methylene groups vibrations).

Interaction of the molecules of this additive and polymer matrix was, like KS films, observed mainly through the N—H stretching vibration bands, where an increase in intensity was observed in the high wavenumbers side (free NH). A shift to lower wavenumbers and a broadening was also observed in the "bonded" NH band ($3330\,cm^{-1}$). The carbonyl region is more difficult to analyze because KS, EDTA-Na as well as the PU matrix have C=O groups in the structure. Unionized and uncoordinated —C(O)O stretching band occurs at $1750–1700\,cm^{-1}$, whereas the ionized and coordinated —C(O)O stretching bands is at $1650–1590\,cm^{-1}$. Therefore the increase in the intensity at higher wavenumbers of the band centered at $1713\,cm^{-1}$ should be assigned to COOH groups and those at 1640 to the ionized COO groups.

The C—O—C moiety of polyetherdiol, composing the soft segments, at $1097\,cm^{-1}$ in the pure PU, shifted to $1110\,cm^{-1}$ in the doped film, indicating interaction through the formation of H-bonds between the COOH of EDTA and the C—O-C groups of PU.

These changes shows that the anionic part of the ionic additives incorporated into the PU matrix associate mainly with the C=O groups throughout hydrogen bonds and compete with the NH groups for this interaction places located in the hard segments, generating "free" NH groups, but with no significant changes the quantity of both free or bonded C=O groups.

This observation agrees with the SAXS data discussed above, the formation of new H-bond with EDTA or KS generate new aggregates which contribute with the increase of the signal at low q values.

### 3.3. Differential scanning calorimetry (DSC)

The DSC curves in polyurethanes are often difficult to interpret because many transitions occur as a result of partial separation

**Table 1**
Thermal events found in PU and active films.

| | Additive (wt.%) | $Tg_I$ | $Tg_{SS}$ | $T_I$ | $T_{II}$ ($E_I$–$E_{II}$) | $T_{III}$ |
|---|---|---|---|---|---|---|
| PU | – | n/d | −28.5 | 51 | 147–177 | 225 |
| Toc | 1 | −73.3 | −29.2 | 50 | 142–177 | 242 |
| | 2 | −72.3 | −28.1 | 49 | 140–178 | 242 |
| | 5 | −70.1 | −38.7 | 49 | 144–171 | 242 |
| BHT | 1 | n/d | −30.8 | 44 | 137–167 | 226 |
| | 2 | n/d | −31.8 | 42 | 144–165 | 221 |
| | 5 | n/d | −28.8 | 41 | 137–171 | 225 |
| KS | 0.5 | −61.1 | −35.3 | 45.5 | 146–173 | 216 |
| | 1 | −61.8 | −35.7 | 46.3 | 136–174 | 215 |
| | 2 | −66.8 | −33.7 | 45.3 | 140–174 | 217 |
| EDTA | 0.5 | n/d | −35.4 | 43.6 | 143–170 | n/d |
| | 1 | n/d | −35.2 | 43.2 | 138–170 | 220 |
| | 2 | n/d | −36.6 | 42.1 | 138–176 | 218 |

in hard segments (HS) and soft segments (SS). Thus, they may present first-order transitions (melting, $T_m$) and glass transitions, $T_g$, for each of these segments, in addition to possible crystallization processes, realignment of the polymer chains and disruption of physical links of short or long range.

The PU synthesized in this work showed a glass transition belonging to SS ($T_{gSS}$) at −28.5 °C, and another transition ($T_I$) with a minimum at 51 °C. At higher temperatures a broad endotherm ($T_{II}$) was observed with two minima at 147 °C ($E_I$) and 177 °C ($E_{II}$), and another ($T_{III}$) that started at 225 °C (Table 1). These results indicate that the separation between hard and soft domains is not complete, which can be seen by observing the $T_{gSS}$, which appear at higher temperature than that for the PPG moiety ($T_g \approx −70$ °C), indicating an affinity and interaction to hard domains, which restricts the movement of the soft segments, increasing the value of glass transition temperature thereof. The transition observed at about 50 °C, has not been clearly defined to what thermal event corresponds to. According to Garrett et al. [15], this transition corresponds to a melting of the soft segments. On the other hand, Choi et al. [16] suggest that although it is not clear the origin of this transition, it cannot be attributed to a process of crystallization of neither soft segments nor hard segments, and propose that this transition is associated, in the systems studied, to a process of spontaneous separation between HS and SS. Similarly, Lee and Hsu [17] note, isothermally at 55 °C to obtain faster phase separation.

Endotherms located between 80 and 230 °C were associated with different disruptions interactions (long and short range) between hard segments and the interface SS-HS, closely related to the percentage of existing hard microdomains in the polyurethane under study. Specifically, an endotherm in the region of 80 °C has been attributed to the dissociation of the hydrogen bonds between the soft and hard segments, whereas an endotherm in the range from 150 to 170 °C was related to the disruption of hydrogen bonds between rigid domains [18].

In films with Toc, two transitions were observed at temperatures below zero. The first was located between −73 and −70 °C, corresponding to the flexible segments of the polyol, according to the $T_g$ observed for pure PPG (−70 °C), while the other transition (about −30 °C) correspond to the $T_{gSS}$. The separation of the $T_{gSS}$ into two transitions in Toc-doped films can be explained in two ways. One possible explanation is that the additive promotes the segregation of SS and HS microdomains, and thus allows some of the soft segments to be grouped together originating the Tg around −70 °C. Another possible explanation is that Toc molecules are among the "most open" SS, exerting a plasticizing effect on a portion thereof. The latter hypothesis would be strengthened by the IR and SAXS data.
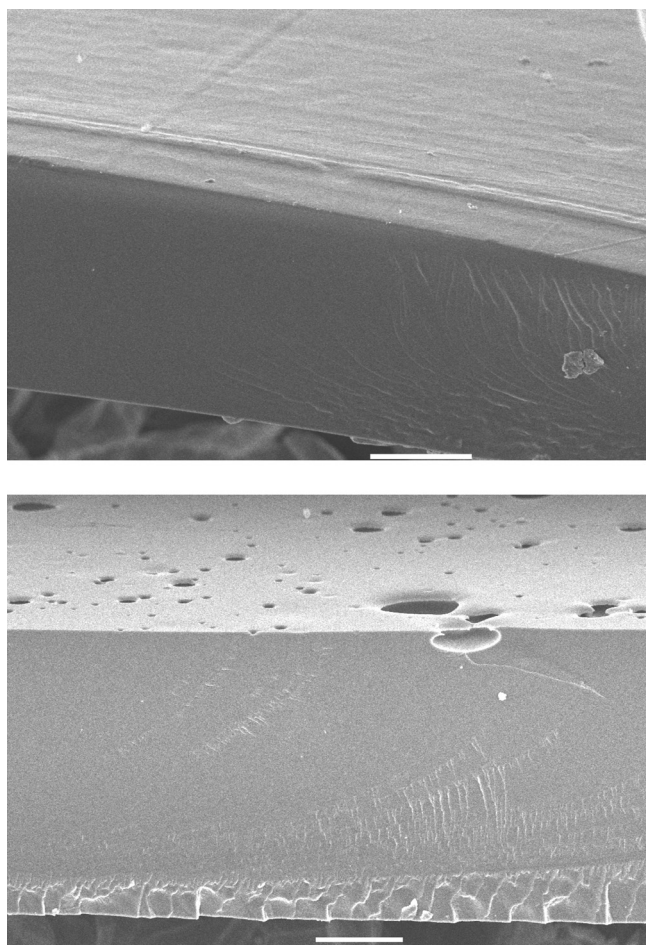
**Fig. 4.** SEM images of PU (top) and Toc2 (bottom) films. Bars = 50 μm.

**Table 2**
Mechanical properties in PU and active films.

| | Additive (% Wt) | Stress at break (MPa) | Elongation at break (%) | Stress Modulus (MPa) |
|---|---|---|---|---|
| PU | – | $19.0 \pm 1.4$[a] | $400 \pm 22$[a] | $47.0 \pm 2.9$[a] |
| BHT | 1 | $17.1 \pm 0.5$[a,b] | $370 \pm 12$[a,b] | $42.4 \pm 2.3$[a,b] |
| | 2 | $17.0 \pm 0.7$[a,b] | $369 \pm 17$[a,b] | $40.7 \pm 2.1$[b] |
| | 5 | $14.8 \pm 0.9$[c] | $360 \pm 13$[b] | $39.3 \pm 2.0$[b] |
| Toc | 1 | $16.4 \pm 1.1$[b,c] | $326 \pm 17$[c] | $41.6 \pm 2.8$[b] |
| | 2 | $15.7 \pm 1.0$[c] | $337 \pm 22$[b,c] | $38.4 \pm 3.1$[b] |
| | 5 | $11.5 \pm 1.9$[d] | $273 \pm 28$[d] | $28.7 \pm 3.3$[c] |
| KS | 0.5 | $18.3 \pm 0.2$[a] | $408 \pm 9$[a] | $38.0 \pm 2.2$[b] |
| | 1 | $18.1 \pm 0.9$[a,b] | $403 \pm 4$[a] | $43.0 \pm 1.0$[a,b] |
| | 2 | $16.7 \pm 0.8$[b,c] | $377 \pm 16$[a,b] | $36.9 \pm 1.8$[b] |
| EDTA | 0.5 | $17.9 \pm 0.6$[a,b] | $434 \pm 26$[a] | $46.3 \pm 2.9$[a] |
| | 1 | $17.7 \pm 0.6$[a,b] | $388 \pm 28$[a,b] | $47.5 \pm 3.3$[a] |
| | 2 | $14.8 \pm 0.2$[c] | $369 \pm 16$[a,b] | $44.8 \pm 4.5$[a,b] |

Means with different letters, in the same column, indicate significant differences ($p < 0.05$).

The $T_I$ transition, located at 52 °C for PU, was not altered by the addition of α-tocopherol at the concentrations studied, accounting for a poor interaction between the additive and partially crystalline domains of the SS matrix, indicating an additive preference for the amorphous domains.

When BHT was added, the $T_{gSS}$ value was not substantially modified at any of the concentrations studied, but a widening of the transition was observed with the increase of percentage of additive added. The first endotherm (at 147 °C in PU) was still less intense and even not possible to observe it in the BHT 1 and 5% samples, while the second endotherm (177 °C in PU) was found at a lower temperature and it was narrower than in PU, indicating some BHT effect on the long-range interactions in the hard segments, confirming the fact that the additive is placed between the polymer chains, binding to the carbonyl groups by hydrogen bonding and breaking the HS inter or intrachain interactions.

In the films with potassium sorbate, $T_{gSS}$ and $T_I$ temperatures were around −35 °C and 45 °C respectively; both were about 8 °C lower than those obtained for pure PU. Similarly to what occurred in the films with α-tocopherol, a transition at temperatures of −67, −62 and −61 °C, for KS 2, KS 1 and KS 05, respectively were observed.

The transitions attributed to the hard segments, were presented in a similar way to those obtained for PU film, but with lower values of △H, multiple endotherms disappearing within them.

In films with EDTA-Na no thermal transition was observed at temperature near −70 °C, however, the breadth of the $T_{gSS}$ is much larger than in the PU ranging between −60 °C and −5 °C; in the polyurethane, this range of △T is about 30 °C. A transition is made wider when the polymer chains that undergo the transition, present heterogeneities. Thus, and as it was observed by FT-IR, it can be said that EDTA ions affect the order and the interactions of the soft segments of the polyurethane. The transition called $T_I$ is also modified by the percentage of EDTA-Na added. In transitions assigned to hard domains, it is noted that the temperatures and the value of △H are similar to those corresponding to the films with potassium sorbate.

These data are consistent with those observed by IR spectroscopy and SAXS, as the EDTA moieties preferentially interact with the soft segments (through hydrogen bonds with the oxygen of the ether group), and the sorbate ions with both, soft and hard domains.

### 3.4. Scanning electron microscopy (SEM)

Films surface morphology observed by SEM showed a different behavior for films doped with α-tocopherol respect to the PU film and the films containing the other additives. As expected, PU film showed a continuous and smooth surface (Fig. 4, top), owing to the low $T_g$ value and the good film forming capacity of these systems [19]. While BHT, KS and EDTA-Na films maintain these characteristics (images not shown), Toc-doped films presented holes and irregularities all over the surface (Fig. 4, bottom) and these defects increased with the additive content on the film. This behavior is due to the phase separation, during drying, of the hydrophobic α-tocopherol that migrates to the air-side surface of the film, avoiding in this way the interaction with the (water) polar environment. It was confirmed by the observation of the substrate surface, which showed no defects. Cross-section images (Fig. 4) confirmed the compact and non-porous structure of the PU, and the presence of pores and capillaries channels in the Toc doped films.

### 3.5. Mechanical properties

The stress modulus values of the films are slightly diminished (about 10% compared with PU) with the incorporation up to 2 wt.% of BHT in the polyurethane matrix, as can be seen in Table 2.

Films containing potassium sorbate presented, up to 1 wt.% of concentration, values of stress tension and elongation at break similar than PU film, while stress modulus is lower. On the other hand, EDTA-Na films had similar tension modulus than PU, but lower stress tension and elongation at break. As shown below, phase separation of Toc-incorporated films, makes mechanical resistances greatly diminished.
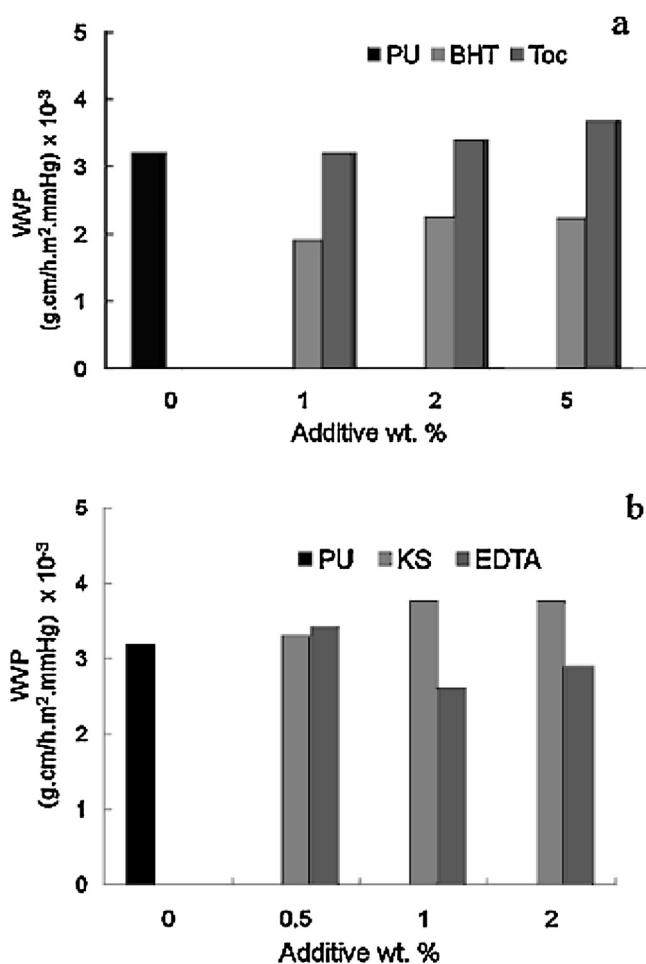
**Fig. 5.** Water vapour permeability in PU and active films. a) BHT and Toc, b) KS and EDTA.

Even if exists a reduction in the mechanical properties of active films compared with pure PU systems, films with antioxidant or antimicrobial activity were obtained and are able to use as packaging or coating systems without substantially sacrificing mechanical properties.

### 3.6. Water vapor permeability (WVP)

Permeability of a polymer film could be modified by changes in the formulation of the matrix or by adding different additives thereto. Thus, it has been found that the addition of clays or other compounds decrease the WVP of the nanostructured polymer film due to the effect of "tortuosity" imposed to the passage of water molecules through the material [20]. Furthermore, the addition of hydrophobic compounds into a polymeric matrix could generate, if they are homogeneously distributed in the film, a barrier effect to the passage of water molecules [21]. Particularly, in polyurethane systems, changes in inter or intra-segment interactions promoted by these additives would be also important. WVP values obtained for PU and active films are shown in Fig. 5. In BHT films lower permeability values than those obtained for control (PU) films were observed, with no-significant effect of the additive percentage incorporated. On the other hand, α-tocopherol incorporated films showed an increase of WVP values with the addition of the antioxidant (Fig. 5a). These results indicate that the BHT produces a "barrier" effect through their homogeneous distribution in the film. Otherwise, as α-tocopherol is partially secreted in the samples, small pores observed in SEM images (Fig. 4 bottom) favor

the passage of water molecules producing an increase in the WVP. Therefore, the presence and number of this pores act opposite to the hydrophobic barrier created by the additive, controlling the observed WVP behavior of these samples.

It is expected that the addition of polar additives with hydrophilic nature to the polymer matrix generates, in principle, an increase in the hydrophilicity of the same, leading to an increase in the water vapor solubility in the polymer, which increase the WVP according to the equation P = D.S, where D is the diffusion coefficient and S the permeant solubility in the polymer. Also, as discussed earlier, the interaction of the additives with hard and/or soft segments of the polyurethane and the disruption or generation of links within the matrix induced by the additive, cause changes in permeability properties of the resulting films.

KS active films presented WVP values higher than that observed for control films, while EDTA1 and EDTA2 films showed permeability values below the obtained for PU (Fig. 5b). The KS effect observed in WVP is expected, as discussed above, for the important hydrophilicity of the additive, meanwhile in EDTA1 and EDTA2 films the decrease observed in WVP could be related to a physical crosslink effect led by the carboxylate/carboxylic groups of the EDTA molecule interacting with the electronegative atoms in the soft or hard segments (see FT-IR discuss), however this crosslinking effect could not be observed as an increase of the mechanical properties of EDTA samples respect to PU (Table 2).

### 3.7. Water swelling degree

Fig. 6 shows the water swelling kinetics for control and doped PU films. PU film showed a quasi-Fickian behavior, reaching the saturation value of water absorption of about 40 wt.% after 18 days.

Both EDTA-Na and KS are hydrophilic compounds; therefore, an increase in its concentration inside the polymeric matrix favors the water incorporation into the film and then the migration across it. The films doped with 0.5 wt.% of these active compounds, showed a similar behavior compared to the pure PU matrix but the saturation was reached in a shorter time (4–5 days), therefore the water incorporation to the film is faster than in the pure film. However, films with 1 and 2 wt.% of active compound present very different water absorption kinetic when comparing to the control film. These dynamics swelling curves exhibit an "overshooting effect", that is, the curves show a maximum followed by a gradual decrease until the equilibrium is reached. In the films doped with 2 wt.% of potassium sorbate, it was observed a very pronounced increase in the value of water absorption, absorbing in 5 h almost 60% of water, followed by a fast desorption, reaching a steady value of 22% at 8 days. In the film doped with 1 wt.% of KS, this behavior was less pronounced, obtaining the maximum value of absorption (approximately 42%) after 24 h and reaching the steady value of 28%, also in 8 days (Fig. 6a).

This swelling-deswelling behavior known as "overshooting effect" in polymer matrixes has been reported early in the 1980′s [22,23] for non-polar solvents; later for hydrophilic non-ionic solvents [24–26], and more recently for water and aqueous solutions [27–30]. This swelling kinetic behavior has not been explained unambiguously, neither the kinetics nor the transport mechanism process [28]. Peppas and co-workers [22–24] attributed this behavior to the relaxation process of the polymeric chains. Ionic crosslinking [31] and a cooperative physical and chemical crosslinking effects caused by the formation of hydrogen bonds [28] were also other explanations. Díez-Peña and co-workers [28] has recently gave a quantitative kinetic model for the explanation of the overshooting effect in poly(N-iPAAm-co-MAA). According to this model, the first water uptake of the initial hydrophilic gel is followed by the transportation of this gel into a more compact and hydrophobic cross-linked structure with a lower swelling capac-
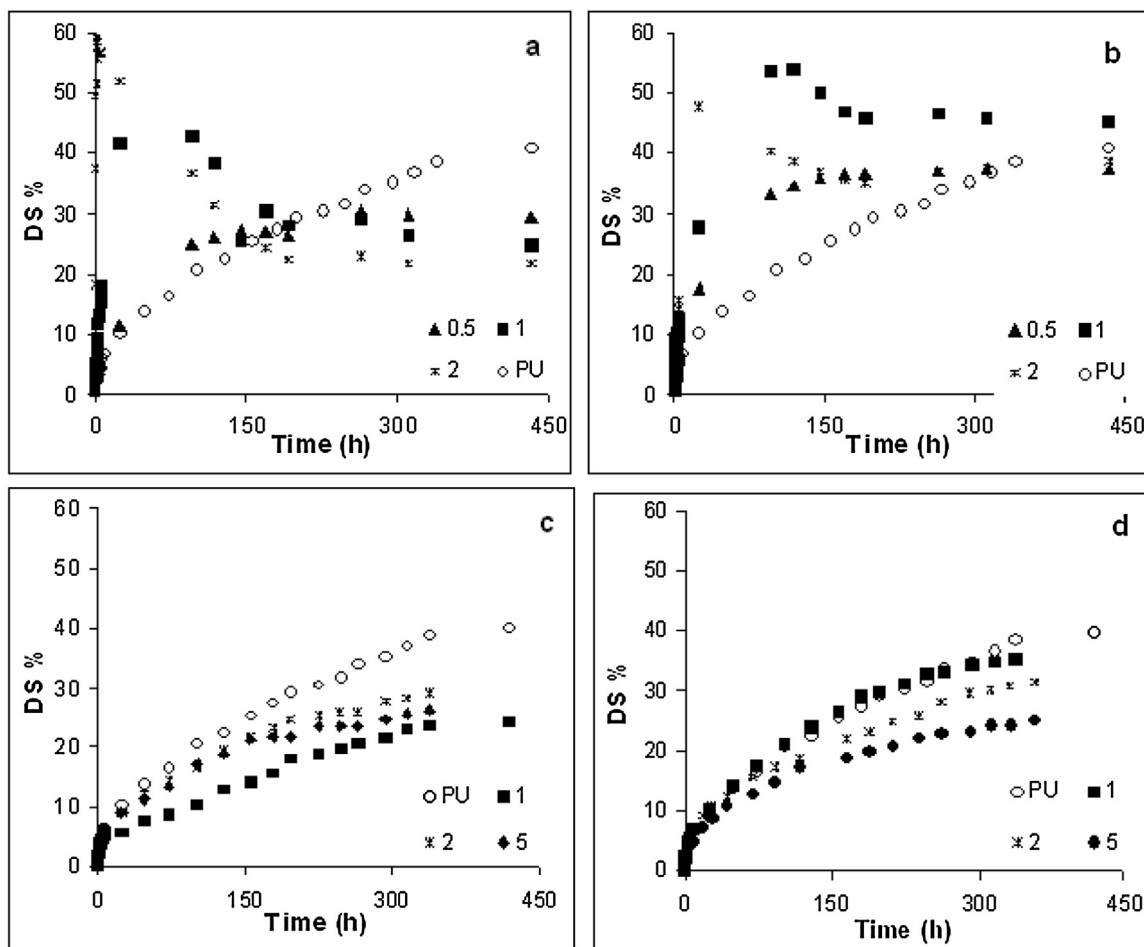
**Fig. 6.** Swelling degree (%) in PU and active films. a) KS, b) EDTA, c) BHT, d) Toc.

ity, and finally the water is expelled until the new equilibrium is reached.

It is important to note that for higher KS concentration, the final value of water absorption was lower than that obtained for films with 0.5 and 1 wt.%; on the other hand, the maximum value that was registered in the assays relates directly to the quantity of added additive. The final value of water absorption for these KS-doped films was significantly lower than the pure PU control film.

The EDTA-Na doped films presented a similar behavior but, unlike KS, the water desorption after reaching the maximum value, was not so noticeable, reaching an equilibrium value of among 38–45 wt.%, a similar one to the obtained for the pure PU matrix (Fig. 6b).

Polyurethane matrix having in its structure proton donors and acceptors can interact through strong specific bonds in aqueous solutions. The incorporation of a high hydrophilic compound into the polymeric matrix, as the salt of an organic acid, will increment the water uptake in the early stages, due to osmotic effect.

This first step of water incorporation favors the chain relaxation and allows a new rearrangement and interaction between them. This interaction given by dynamic hydrogen bonds formation will produce the de-swelling effect in these films. The water expulsion that happens in the de-swelling can drag the additive molecules, enhancing the interaction between the polymeric chains.

According to Díez-Peña et al. [27,28], the overshooting effect cannot be explained just by the assumption of different rates of diffusion and simple molecular chain relaxation effects. Some types

of chemical or physical interactions might control such relaxation effects.

As seen in Fig. 6c and d the water-swelling ratio is also modified by the incorporation of the antioxidant additives (BHT and α-tocopherol) to the polyurethane matrix. However, an overshooting effect is not evidenced. When the active component is α-tocopherol, the relation between percentage of additive and the decrease on the swelling capacity is more evident than when the incorporated additive is BHT. Again, the α-tocopherol molecules could form aggregates, which would create more hydrophobic zones; on the other hand the BHT is homogeneously distributed on the film, making the water swelling lower regardless of the concentration.

Taking into account the potential application of these systems as active films, effectiveness of the antioxidant action of the films studied in this work, as well as its diffusional behavior were recently studied [32].

## 4. Conclusion

SAXS, FTIR and DSC studies of segmental polyurethanes films show that addition of additives results either in the formation of aggregates or modification of the polymer microstructure, depending of the molecular size and nature of additive. The non-polar additive butylatedhydroxytoluene modifies the microstructure of polyurethane, but molecules of α-tocopherol seem to be too big to accommodate between polyurethane chains and phase segregation is observed. Ionic additives like potassium sorbate and the dis-

odium salt of the ethylendiaminetetracetic acid changes the SAXS curves in the low wavevector region, suggesting an increment in the local electronic density and/or in the interdomain distances.

When the films are immersed in water, different situations were observed with the different additives. EDTA-Na and KS swelling kinetics show an anomalous behavior interpreted as a swelling–deswelling process, attributed to a modification of the PU matrix structure due to the hydrogen bond formation between the polymeric chains and the additive molecules and the reorganization after the water swelling (overshooting effect). BHT and Toc films show a quasi-Fickean behavior, as well as pure PU films, with a decrease of the water uptake when increasing the antioxidant content. Briefly, the addition of food additives to the PU dispersion produces morphological changes in the films formed therefore. Those modifications, in addition to the effect of the additive itself, affect the mechanical and transport properties of the material. The decrease in some of these properties is the drawback for obtaining a polyurethane active film.

## Acknowledgements

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