Effect of Essential Oils in the Properties of Cellulosic Active Packaging

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Summary: The use of essential oils (EO) as antifungal agents is an alternative to synthetic fungicides. In the present work, active packaging in the form of cellulosic films and paper coated with a cellulosic emulsion incorporated with 20% cinnamon, oregano or lemongrass EO was developed. The mechanical properties (maximum load-at-break and elongation at break), the water-vapor-barrier properties and the microscopic characterization of the packaging materials were evaluated. The EO added to the packages significantly affected the maximum load at break of the active films and their elongation at break. The EO incorporated in the films and coated paper did not affect the water-vapor barrier. However, this parameter was significantly modified when the uncoated paper and coated paper with and without EO were evaluated. The incorporation of EO altered the microstructures of the active films and coated paper.

Keywords: biopolymers; coating; films; food packaging; mechanical properties; water-vapor barrier

Introduction

Consumer health concerns and the demand for foods free from additives have motivated the scientific community to search for new food-conservation methods.[1] In the last years, several techniques of post-harvest conservation have been used to guarantee the preservation, freshness and quality of foods.[2] As a result, new methods of food preservation are being studied and developed to maintain the quality of the product for a longer shelf life.[3,4]

Natural substances such as essential oils (EO) have been long recognized for their antibacterial, antifungal, antiviral, insecticidal and antioxidant properties:[5,6] they are characterized as volatile oily liquids obtained from various plant parts and are widely used as food flavor.[7]

The use of essential oils (EO) is an alternative to the use of fungicides because these substances have antimicrobial properties.[8–10] Moreover, the EO are designated as generally regarded as safe (GRAS).[7] The EO can contain more than sixty individual components[11] and the major components can constitute up to 85% of the EO, whereas other components may be present only in trace amounts.[12] The major components in cinnamon, oregano and lemongrass EO are trans-cinnamaldehyde (65%), carvacrol (80%) and citral (this one constituting 69% and composed by neral and geranial isomers), respectively, and they are mainly responsible for the antibacterial properties of EO.[7,13–14] However, some evidence indicates that minor components of EO play a critical part in their overall antibacterial properties, possibly by producing a synergistic effect between components. Hence, the use of these natural substances as possible substitutes for commercial fungicides and the possibility of their incorporation into packaging material has been considered.[3,15]

Antimicrobial substances incorporated into a polymeric matrix have an important function in packaging because they are another barrier to microbial growth and

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contribute to food preservation. Thus, the study of the resistance of packaging materials to maximum load and elongation parameters is important because these parameters describe the mechanical and structural properties of the packaging material.[16] Furthermore, the evaluation of the water-vapor barrier is also necessary because many food products are susceptible to humidity.[17] Therefore, as the EO have potential applications in active packaging, it is necessary to study the effects of such substances when incorporated into a polymeric matrix.[18] The aim of this work was to study the effects incorporating oregano, cinnamon or lemongrass EO on the mechanical properties, water-vapor barrier and microstructure of the developed active packaging materials.

Experimental Part

Materials

Cellulose acetate (Rhodia, Freiburg, Germany), acetone (Vetec®, RJ, Brazil) and vegetable parchment (50 $g \cdot m^{-2}$) were used for the elaboration of the active films and coated paper. Oregano, cinnamon, or lemongrass EO were incorporated at concentrations of 20% (w/w). This concentration was selected according to previous studies on the antifungal properties of these EO.[19]

Active Packaging Elaboration

The active paper was produced using the methodology proposed by Rodríguez et al.[20] with some modifications. The filmogenic solution, which consisted of cellulose acetate and acetone (1:20), was supplemented with 20% (w/w) of oregano, cinnamon or lemongrass EO. The percentage of the EO was in relation to the total weight of the packaging material. The EO were added individually, one at time, into the filmogenic solution. The control treatments were paper without coating and coated paper with the cellulosic emulsion but without EO incorporation. The active films were obtained by the casting method described by Soares.[21] The cellulose was dissolved in acetone, and after solubilization, the EO was incorporated into the cellulosic emulsion at a concentration of 20% (w/w) of the cellulose weight. The filmogenic solution was spread and dried at room temperature ($24 \pm 1\,^{\circ}C$), allowing complete evaporation of the solvent. The control film was elaborated by the same method, but without incorporating EO.

In total nine, packaging materials were evaluated as follows: three control materials, which were film without EO, uncoated paper and coated paper without EO; and six active materials, three active paper and three active films (one EO for each material).

Mechanical Properties and Water-Vapor Barrier of the Active Packaging

The thickness (mm) of the active films and coated paper incorporating 20% EO were characterized by measurement with a manual micrometer (precision: 0.01 mm; South America, Mitutoyo, Suzano, SP, Brazil) in random positions and then submitted to mechanical tests for the evaluation of their resistance at the maximum load and elongation according to ASTM[22] methods using the Universal Material Testing Machine (INSTRON Corporation, Norwood, MA, USA). Ten specimens of each treatment (10 cm in length and 2.5 cm wide) were tested. The machine was operated with a load of 1 kN and with a traction speed of 5 mm/min.

The water-vapor transmission of the active packaging material was determined by the gravimetric method according to ASTM[23] with a 75% relative humidity at room temperature ($24 \pm 1\,^{\circ}C$).

Microscopic Characterization

The microscopic characterization of the packaging material (active film and coated paper) was made at the Microscopy and Microanalysis Center at Federal University of Viçosa. A Scanning Electron Microscope (SEM - LEO Electron, Cambridge, England) was used to monitor the surface topology of the developed active packaging materials. The samples ($0.5\,cm^2$) were fastened with stubs and covered with a gold layer (20 nm thick) in the metallizer SCD 010 (Balzer Union, Furstentum, Lichtenstein). Then, the samples were put into holders for SEM examination and microphotography capture.

Results and Discussion

Mechanical Properties and Water-Vapor Barrier of the Active Packaging

The thickness values of the active films and coated papers did not demonstrate significant differences ($p > 0.05$) among the treatments (Table 1).

The maximum load-at-break values for the active films incorporating cinnamon or oregano EO demonstrated significant differences ($p < 0.05$) from those of the control film. The highest value of maximum load-at-break observed was for the control film (64.02 ± 1.51 N) and this value decreased when the film was incorporated with each EO (Figure 1). The addition of lemongrass EO resulted in the smallest value of this parameter (40.63 ± 2.22 N). Though the mechanical properties of polymers are a consequence of their high molecular masses, the essential oils have low molecular mass[7], so the chemical constituents of the EO interact with the polymeric chains of the film and decrease the values of the mechanical properties of cellulose acetate. This decrease probably results from the EO, which acted as a plasticizer and reduced the resistance at the maximum load.

The values of maximum load-at-break found for the coated paper incorporating oregano EO and the uncoated paper were significantly different (Figure 1). However, this parameter did not present significant differences ($p > 0.05$) among the coated papers that contained the tested EO. Hence, the uncoated paper displayed a notably smaller maximum load-at-break value (35.07 ± 1.10 N) in comparison to the other treatments. We can attribute this performance to the synergistic resistance of the paper with that of the cellulosic coating. McHugh et al.[24] explain that films developed from fruit purées do not have good mechanical properties; however, when other substances such as alginate are added, they demonstrate better results.

The active films and coated papers were characterized with respect to the elongation at break. The results showed significant differences ($p < 0.05$) for this parameter when the films incorporated with EO were compared to the control film (Figure 2). The incorporation of the different EO in the films resulted in a significant increase in the elongation values; the elongation of the films with oregano ($10.9 \pm 1.6\%$) and lemongrass EO ($11.7 \pm 2.8\%$) was much greater than that of the control films, which demonstrated the smallest value for this parameter ($4.6 \pm 2.1\%$).

These results indicate that the largest flexibility and elongation capacity of the polymeric matrix occurred when EO was incorporated. Similar results were obtained by Rojas-Graü et al.[25], who observed an increment in the elongation percentage in films of alginate and apple purée added with oregano, cinnamon and lemongrass EO. However, this parameter did not present significant differences ($p > 0.05$) for the coated paper, which indicates that the incorporation of EO did not have an effect on the elongation of the packaging

Table 1.
Thickness values (mm) of the packaging materials evaluated.

Packaging Material		Control	EO		
			Oregano	Cinnamon	Lemongrass
Film		0.045 ± 0.005	0.042 ± 0.002	0.045 ± 0.001	0.043 ± 0.001
Paper	Uncoated	0.042 ± 0.002	0.040 ± 0.005	0.041 ± 0.001	0.041 ± 0.001
	Coated	0.042 ± 0.002			

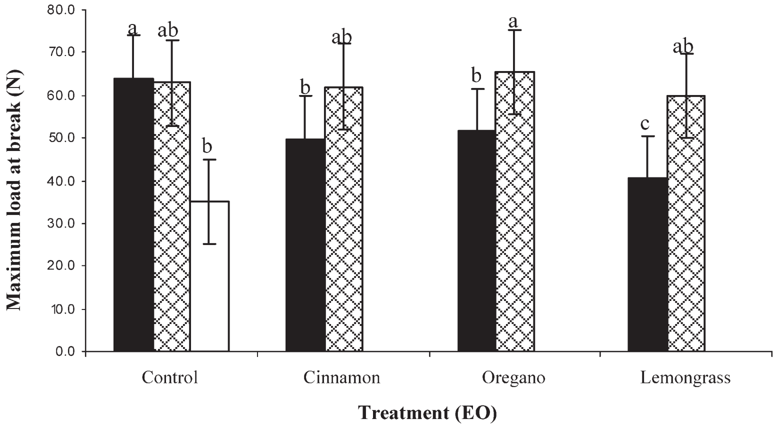

Figure 1.
Maximum load-at-break (N) for active film (■), coated paper (☒) and paper without coating (□). The same letters for the same packaging material indicate no significant difference ($p > 0.05$) by the Tukey test.

material in the different treatments; thus the cellulosic matrix was not altered.

The results of the water-vapor-transmission rate (WVTR) analysis did not present significant differences from the controls ($p > 0.05$) among either the films or the coated papers incorporating EO (Figure 3).

The results of this work are consistent with those obtained by Rojas-Graü et al.,[25] who indicated that the incorporation of oregano, cinnamon and lemongrass EO did not affect the WVTR of alginate-based films. In contrast, the WVTR of the coated papers showed significant differences ($p < 0.05$) in relation to that of the uncoated paper. The paper without a coating demonstrated the largest WVTR ($1.264\,g{\cdot}m^{-2}{\cdot}day^{-1}$). The value of this parameter decreased when we evaluated the papers coated with and without EO. This decrease might be a result of the presence of the cellulosic coating with or without EO, which constitutes another barrier against the transmission of the water vapor through the packaging material. In this context, Mancini & McHugh[26] demonstrated the

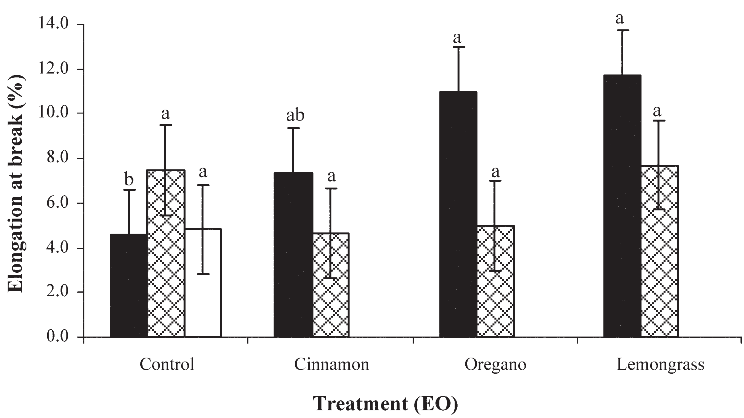

Figure 2.
Elongation at break (%) for active film (■), coated paper (☒) and paper without coating (□). The same letters for the same packaging material (film and paper) indicate no significant difference ($p > 0.05$) by the Tukey test.

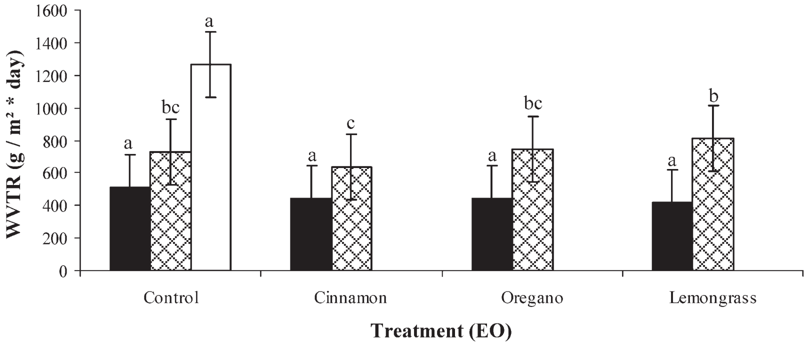

Figure 3.
Water-vapor-transmission rate (WVTR) for active film (■), coated paper (☒) and paper without coating (□). The same letters for the same packaging material (film or paper) indicate no significant difference ($p > 0.05$) by the Tukey test.

improvement of the water-vapor-barrier property of films with the addition of composites such as alginates.

Microscopic Characterization

Figure 4 and 5 show the microphotographs of developed active films and coated paper. The formation of dispersed acetate agglomerates was observed on the surface of the control film and in the sample traverse cut (Figures 4.1.a and 4.1.b). These acetate agglomerates were observed at a smaller size but in a larger amount in the films incorporating oregano cinnamon or lemongrass EO (Figure 4.2.a, 4.3.a and 4.4.a). We can attribute this fact to the incomplete solubility of the acetate in the solvent.

According to the elongation-at-break results, the small values of this parameter in the control film polymeric matrix might be a result of the presence of acetate agglomerates, as observed in the micrographs (Figure 4.1.a and 4.1.b), which were larger than those we observed in the films that contained EO. The size of these agglomerates might have influenced the elongation-at-break values of the films with EO, allowing them to be more flexible and the presence of the EO in the polymeric matrix might have caused a plasticizing effect in the films.

The uncoated paper had disoriented fibers and a great number of pores in the surface (Figure 5.1.a), whereas the surfaces of the papers coated with cellulosic emulsion, with or without EO, had a less porous structure as a result of the coating (Figure 5.2.a, 5.3.a, 5.4.a and 5.5.a) and

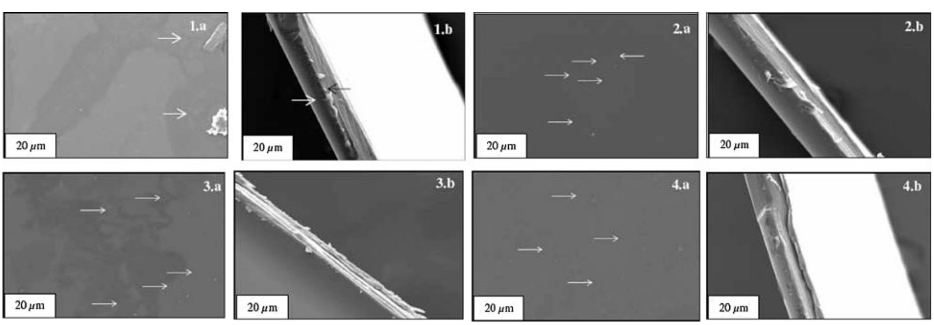

Figure 4.
Microphotography (1,000X) of control film (1.a and 1.b) and films incorporated with oregano (2.a and 2.b), cinnamon (3.a and 3.b) and lemongrass EO (4.a and 4.b). Here, *a* indicates the superficial topography and *b* indicates lateral topography of the film.

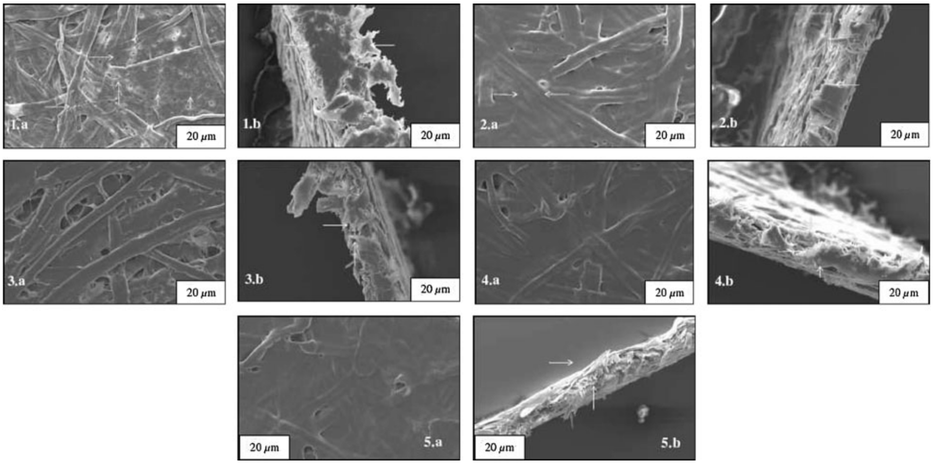

Figure 5.
Microphotography (1,000X) of uncoated paper (1.a and 1.b), coated paper without EO (2.a and 2.b) and coated paper with oregano (3.a and 3.b), cinnamon (4.a and 4.b) and lemongrass EO (5.a and 4.b). Here, *a* indicates the superficial topography and *b* indicates lateral topography of the film.

with more uniform and dense layers formed by the cellulosic emulsion on the paper fibers (Figure 5.1.b, 5.2.b, 5.3.b, 5.4.b and 5.5.b).

Conclusion

The incorporation of oregano, cinnamon and lemongrass EO affected the values of maximum load and elongation at break for the active packaging films. However, these parameters did not present significant differences for the coated paper to which we added EO. The incorporation of EO in the film and the coating on the paper altered their microstructures, presenting changes such as the presence of acetate agglomerates and a less porous structure in the coated paper, as observed in the micrographs. The incorporation of the different EO in the films did not affect the WVTR. However, this parameter decreased when we coated the paper with cellulosic emulsions that either had or lacked EO. Therefore, the incorporation of EO in the polymeric matrix has a potential application as an active packaging material because these substances had no effect on the evaluated properties of the coated paper and films.

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