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Antimicrobial packaging based on linear low-density polyethylene compounded with potassium sorbate

Nataliya Kuplennik [a, b], Roza Tchoudakov [a], Zohar Ben-Barak Zelas [c], Arie Sadovski [d], Ayelet Fishman [c, *], Moshe Narkis [a, *]

[a] Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, 3200003, Israel
[b] Interdepartmental Program in Polymer Engineering, Technion-Israel Institute of Technology, Haifa, 3200003, Israel
[c] Department of Biotechnology and Food Engineering, Technion-Israel Institute of Technology, Haifa, 3200003, Israel
[d] Plasto Sac Ltd. Yavne, 8122201, Israel

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ABSTRACT

In recent years much attention has been devoted to active packaging technologies that offer new opportunities for the food industry and food preservation. In the present study, antimicrobial films were developed by compounding of a neat linear low density polyethylene (LLDPE) or its blend with ethylene vinyl acetate (EVA), with potassium sorbate (KS). A new approach for preservative incorporation into a polyolefin matrix was used to obtain uniform dispersions of the preservative in the films. This approach includes using glycerol monooleate (GMO) as a dispersant and preparation of GMO/KS concentrate by strong mechanical mixing. The antimicrobial activity of the films was studied using the yeast strain *Saccharomyces cerevisiae* S288C. All compositions of LLDPE or LLDPE/EVA containing GMO and KS demonstrated antimicrobial activity. Release tests showed that KS migrates from compression molded 300 μm films to an acidic food simulant and its diffusion is controlled by the Fickian diffusion rule. Thermal stability, rheological behavior, morphology and KS dispersion in the polymer matrices of the prepared blends and films were investigated. The results indicate that the presence of KS in the polymer matrix significantly improves the thermal stability of the blends compared with the neat matrices without a significant viscosity reduction.

1. Introduction

Preservation techniques for prevention of food spoilage have been practiced since ancient times. Food preservation is a process of treating and handling food to stop or slow down the process of spoilage thus allowing longer storage times. Nowadays, both traditional and modern preservatives are widely used to ensure the satisfactory maintenance of quality and safety of foods (Davidson, Sofos, & Branen, 2005). In most, but not all solid or semisolid foods, microbial growth occurs primarily on the surface and therefore preservatives that are mixed directly with the food may result in over-use (Dickson & Anderson, 1992). In order to avoid the over-use of food preservatives and at the same time to maintain the food quality, the concept of antimicrobial active packaging has been implemented. The main idea behind this concept is the incorporation of antimicrobial agents directly into packaging films. Such methods could provide advantages by releasing antimicrobials directly to the food surface where they may be most effective, and could be the answer to consumers' demand for healthy food without preservatives (Brody, Stupinsky, & Kline, 2002).

A wide selection of antimicrobial substances, e.g. organic acids and their salts, fatty acids, antibiotics, antimicrobial peptides, essential oils, bacteriocins, chelators, enzymes, parabens and metals, has been considered to have the potential for use in active food packaging (Suppakul, Miltz, Sonneveld, & Bigger, 2003). Traditional food preservatives' low cost, commercial availability, wide use in food industry and high thermal stability make them attractive antimicrobial agents for active packaging. According to the report "Food Preservatives Market by Types, Functions, & Applications, Trends & Global Forecasts (2011–2016)" (http://www.marketsandmarkets.com, October 2013) amongst all other antimicrobials, sorbates and benzoates hold the major share of the

* Corresponding authors
E-mail addresses: afishman@tx.technion.ac.il (A. Fishman), narkis@tx.technion.ac.il (M. Narkis).

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Nomenclature

C	Concentrate of potassium sorbate and GMO
D	Diffusion coefficient of active agent in the film (m^2/hr)
EDS	Energy-dispersive X-ray spectroscopy
EVA	Ethylene vinyl acetate (copolymer)
GMO	Glycerol monooleate
HRSEM	High resolution scanning electron microscopy
k	Slope of the linear regression of M_t/M_∞ vs. the square root of time
KS	Potassium sorbate
L	Thickness of the film, (μm)
LLDPE	Linear low density polyethylene
LLDPE-g-MA	Linear low density polyethylene grafted maleic anhydride
M∞	Total amount of diffusing substance released from the film at equilibrium, (g).
MFI	Melt flow index, (g/10 min)
MIC	Minimal inhibitory concentration
Mt	The amount of diffusing substance released from the film at time t, (g).
O.D.	Optical density in 600 nm
t	Time, (h)
TGA	Thermal gravimetric analysis
VA	Vinyl acetate

market among the antimicrobials, accounting for nearly 70% of the global food antimicrobial market.

Potassium sorbate (KS) is widely used for inhibiting mold, yeast and some bacterial strains in various foods, including cheese, baked goods, fruits and vegetables, jams and certain meat and fish products (Davidson et al., 2005). There are numerous, sometimes contradicting results published regarding KS incorporation into different polymer matrices. Weng and Hotchkiss (1993) reported that low-density polyethylene films (LDPE) (0.05 mm thick) containing 1.0% w/w sorbic acid were unable to suppress mold growth when brought into contact with inoculated medium. Contradictory results were reported by Han and Floros (1997) who studied the incorporation of 1.0% w/w KS in low-density polyethylene (0.4-mm thick) and found that KS lowered the growth rate of yeast, and lengthened the lag period before the mold growth became apparent. Research published by Devlieghere, Vermeiren, Jacobs, and Debevere (2000) revealed that ethylene vinyl alcohol/linear low-density polyethylene (EVOH/LLDPE) film (70 μm thick) compounded with 5.0% w/w KS is unable to inhibit the growth of microorganisms on cheese and thus to extend its shelf life probably due to limited migration of the antimicrobial agent from the polymer. Vartiainen, Skytta, Enqvist, and Ahvenainen (2003) studied antimicrobial properties of LDPE and other commercial polymers containing traditional food preservatives sodium benzoate, sodium nitrite, KS and sodium lactate at a concentration of 15% w/w. The authors used ground to micron size antimicrobial powders for compounding. None of the samples in that study showed any inhibition against *Escherichia coli*, but all films except sodium lactate-containing samples had high antifungal activity. Hauser & Wunderlich (2011) showed that films coated with a lacquer containing sorbic acid inhibit *E. coli*, *Listeria monocytogenes*, and *Saccharomyces cerevisiae*.

It is known that when organic acids or their salts are used as preservatives, antimicrobial activity is provided by undissociated molecules of the acid which penetrate the microbial membrane (Mani-López, García, & López-Malo, 2012). Subsequently, maximal antimicrobial activity is obtained at pH values below the acid's pKa. Therefore, KS-containing antimicrobial packaging is limited to products that are acidic by nature. The antimicrobial agent has to be free and able to migrate through the polymer matrix in order to be released from the packaging surface and penetrate through the microbial cell membrane. Thus, the release rate is an important parameter that has to be considered when designing the antimicrobial packaging. The present research focuses on the development and characterization of antimicrobial films, based on linear low-density polyethylene (LLDPE) and its blend with ethylene vinyl acetate (EVA) compounded with KS. The aim of the current study is to investigate the correlation between different compounding procedures, films' composition, their physical properties and antimicrobial activity.

2. Materials

Commercial LLDPE, type FP120C, MFI = 1 g/10 min (Nova Chemicals, Calgary, Canada), and its blend with EVA, MFI = 2.5 g/10 min, VA content = 19% (Enimont, Milan, Italy) 70/30 by weight, served as polymer matrices. KS, 99% purity (Sigma Aldrich, Steinheim, Germany), served as the antimicrobial agent in this study. KS was grounded by hand prior to compounding with polymers. For better dispersion of KS in the polymer matrices, a food grade compatibilizer LLDPE grafted maleic anhydride (LLDPE-g-MA) MFI = 1.5 g/10 min, (DuPont Company, Wilmington, USA), and a food grade dispersant commercial glycerol monooleate (GMO), as received, were used.

YPD medium, served as a growth medium for yeasts, was prepared by dissolving 10 g yeast extract (Becton, Dickinson and Company, Sparks, USA), 20 g peptone (Becton, Dickinson and Company, Sparks, USA) and 20 g glucose (Sigma Aldrich, Rehovot, Israel) in 1 L of distillated water. YPD agar plates were prepared by adding 20 g agar (Acumedia, Neogen Corporation, Lansing, MI, USA) to the broth prior to sterilization. Acetate buffer pH 4.2, 9 mmol/L was prepared from ammonium acetate (Merck KGaA, Darmstadt, Germany) and acetic acid (Merck KGaA, Darmstadt, Germany) was used to adjust the pH of the medium. Xylene was used as a solvent

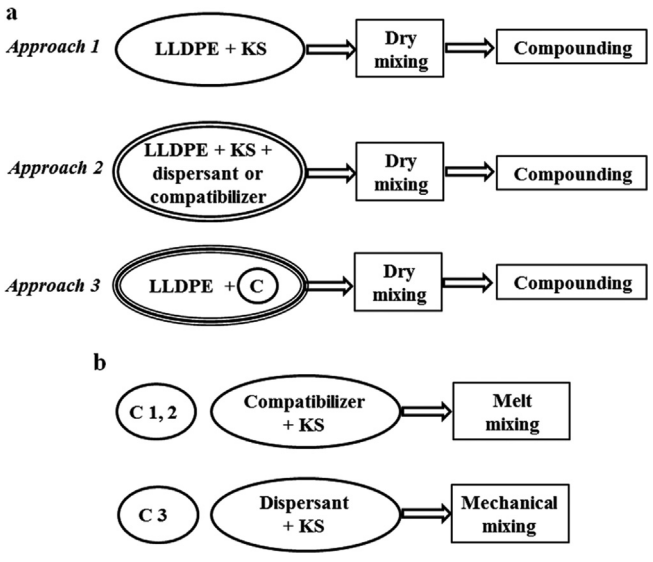

Fig. 1. Scheme of the different approaches used for preparation of the antimicrobial blends. a) Three general approaches comprising dry mixing and compounding, b) Preparation of concentrates containing the antimicrobial agent with the compatibilizer or dispersant. The composition of the concentrates is detailed in Table 1.