

Introduction

Polymer films containing citric acid, sorbic acid, and their salts were produced and positively tested for their antimicrobial potential. The activity against microorganisms could be explained by migration of the active substances out of the material.

Materials and methods

Production of films

- Mixing of the active substances with an ethylene-octene copolymer by extrusion on a laboratory-sized twin-screw extruder at 140 °C
- Pressing to films with ~150-200 µm thickness
- Active substances:
citric acid, mono-sodium citrate,
sorbic acid, potassium sorbate



Haake MiniLab Extruder



Collin P 200 hydraulic press

Microbiological tests

- Spraying of active films and reference LDPE films with bacterial suspension (pieces of 6 x 5 cm, 1 ml of suspension (~10⁴ cells/ml))
- Overlaying with nutritional medium, incubation
- Counting of colonies after 2, 5 and 7 days
- Bacterial strains:
E. coli K-12, Carnobacterium divergens

Migration of active substances

- Food simulants:
water, water/ethanol 9:1 (v/v)
- Two-sided extraction for 7 days at 40, 20 and 4 °C
- Citric acid, citrate: enzymatic test (photometric): citrate lyase, lactate dehydrogenase
- Sorbic acid, sorbate: quantitative thin-layer chromatography after extraction with petrol ether/diethylether 1:1 (v/v), eluent: hexane/acetic acid 96:4 (v/v)

Results and discussion

Microbiological tests

cfu/30 cm² film after 7 days (average of 3 samples)

Citric acid

	LDPE	Copolymer + 15 % citric acid	Copolymer + 25 % citric acid
E. coli	> 200	31	0
C. divergens	98	37	6



LDPE film (left) and copolymer film containing 25 % citric acid (right) sprayed with E. coli after 5 days.

Mono-sodium citrate

	LDPE	Copolymer + 26 % citrate	Copolymer + 51 % citrate
E. coli	> 200	81	0
C. divergens	102	49	2

Sorbic acid

	LDPE	Copolymer + 2 % sorbic acid	Copolymer + 5 % sorbic acid
E. coli	> 200	195	2
C. divergens	> 200	200	8

Potassium sorbate

	LDPE	Copolymer + 20 % sorbate	Copolymer + 30 % sorbate
E. coli	> 200	13	3
C. divergens	> 200	125	13

E. coli is generally more sensitive than Carnobacterium divergens.

Effective inhibition of microorganisms is possible, but (except for sorbic acid) only with very high concentrations of the active substances.

The microbiological results show that these films offer a promising approach for active antimicrobial packaging, but further research and development will be necessary to use the tested films for the packaging of foodstuffs (e.g. meat).

Migration of active substances

Selected results after 7 days, average of at least 2 samples

Citric acid

Migration into water from a film containing 25 % citric acid

	40 °C	20 °C	4 °C
Dissolved citric acid (mg/g polymer)	248.6	235.8	185.2
Dissolved citric acid (% of the originally available substance)	99.4	94.3	74.1

Mono-sodium citrate

Migration into water from a film containing 51 % citrate

	40 °C	20 °C	4 °C
Dissolved citrate (mg/g polymer)	416.5	404.3	361.1
Dissolved citrate (% of the originally available substance)	98.8	95.9	85.6

Citric acid and citrate show very high migration rates. There is only a little difference between 40 and 20 °C, but a rather high differences between 20 °C and 4 °C.

Sorbic acid

Migration at 40 °C from a film containing 5 % sorbic acid

	water	water/ethanol 9:1
Dissolved sorbic acid (mg/g polymer)	6.0	13.8
Dissolved sorbic acid (% of the originally available substance)	11.9	27.5

Potassium sorbate

Migration at 40 °C from a film containing 30 % sorbate

	water	water/ethanol 9:1
Dissolved sorbate (mg/g polymer)	182.8	77.3
Dissolved sorbate (% of the originally available substance)	82.2	34.7

Sorbic acid migrates better into the water/ethanol mixture, potassium sorbate better into pure water.

The migration rates are generally much lower than those of citric acid and mono-sodium citrate, but otherwise the antimicrobiological effect of these substances is much higher.

In any case the migration of the substances offers an explanation for the antimicrobial properties of the films.