

SORPTION BEHAVIOR OF AN ALIPHATIC SERIES OF ALDEHYDES  
IN THE PRESENCE OF POLY(ETHYLENE TEREPHTHALATE) BLENDS  
CONTAINING ALDEHYDE SCAVENGING AGENTS

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University  
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy  
In  
Food Science and Technology

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21 November 2002  
Blacksburg, Virginia

Keywords: Active packaging, Diffusion, Migration, Milk, Off-flavors, Permeation,  
Scalping, Sorption

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**ABSTRACT**

The quality of many beverages and food products is compromised by the presence of low molecular weight aldehydes. Aldehydes are commonly formed during storage by the oxidation of lipids or are introduced as migrants from polymeric packaging material. The objective of this project was to evaluate the effectiveness of three aldehyde scavenging agents, blended into poly(ethylene terephthalate) (PET) films, in removing an aliphatic series of aldehydes from an acidified aqueous model solution (pH 3.6) during storage. Aldehyde concentration in solution was determined by an improved high performance liquid chromatography method involving the formation of aldehyde-hydrazine complexes by 2,4-dinitrophenylhydrazine. Storage of 25  $\mu\text{M}$  mixtures of acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, and caproaldehyde in contact with PET films blended with 5% poly(m-xylylene adipamide) (nylon MXD6), D-sorbitol, or  $\alpha$ -cyclodextrin reduced the concentration of each aldehyde in solution by 21 to 90% after 14 days of exposure. D-sorbitol and  $\alpha$ -cyclodextrin aldehyde scavenging PET films were the most effective treatments for the reduction of aldehydes from solution showing similar average reductions for the five aldehyde species of 11.4 and 13.8  $\mu\text{M}$ , respectively. PET films blended with nylon MXD6 were less effective in removing aldehydes from solution showing an average reduction of 8.4  $\mu\text{M}$  for the five aldehyde species. However, nylon MXD6 proved to be the most efficient aldehyde scavenging agent tested. D-sorbitol and  $\alpha$ -cyclodextrin blends include 45 and 17 times more aldehyde scavenging sites than nylon MXD6 blends, but only showed 26 and 39% improvements in aldehyde scavenging ability when compared to nylon MXD6 blends. Aldehyde scavenging films demonstrated selective scalping preferring smaller molecular weight aldehydes, such as acetaldehyde, propionaldehyde, and butyraldehyde, more than larger aldehydes, valeraldehyde and caproaldehyde. Partition coefficients for smaller aldehydes were 3 to 6 times greater for aldehyde scavenging films than control film.

## **DEDICATION**

This dissertation is dedicated to my wife, Amy Lynn, and my daughter, Ashlyn Taylor. I cannot express in words the love and support each have provided during this project. I am truly blessed to have two such wonderful people to share my dreams.

## ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my major advisor, Dr. Joseph Marcy, for his guidance, constructive criticism, infinite patience, and assistance in completing my research and doctoral studies. I would like to extend further appreciation to my graduate committee members; Dr. Barbara Blakistone, Dr. Susan Duncan, Dr. Timothy Long, and Dr. Sean O’Keefe for their interest, advisement and input throughout my research work.

Very special thanks to Dr. Brian Love and David Brooks for their assistance with the preparation and characterization of finely ground polymeric materials used in this research; to Dr. Foster Agblevor for his help and generous support involving high performance liquid chromatography analysis; to David Williams for his help with differential scanning calorimetry; to Kim Waterman for her help with thermal gravimetric analysis; to John Koontz, Brian Yaun, Wes Schilling, and Marleen van Aardt for their endless support in the laboratory and office; and to Harriet Williams and John Chandler for their constant support. Additionally, I want to recognize Micromeritics Instrument Corp. for their density and surface analysis of polymeric films and powders and Dairy Management Inc. and the Center for Advanced Processing and Packaging Studies for financially supporting this research.

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## LIST OF ABBREVIATIONS AND TERMS

ATR	attenuated total reflection
$A$	surface area of the stationary phase in a chromatographic column
$A$	eddy diffusion in a chromatographic column
$A_a$	molecular area of a molecular probe
$A_{ads}$	area framed by elution time of a non-retained species, posterior peak profile, base line and peak height
$a$	activity of a permeant gas
$a$	uptake of an adsorbed species by the stationary phase
$a_{cal}$	calibration peak area
BET	Brunnauer-Emmitt-Teller method for determining the surface area of a coated inert support stationary phase in a chromatographic column
$B$	longitudinal diffusion in a chromatographic column
$b$	affinity of gas molecules to get sorbed into voidage areas in polymer
CPMAS	Cross Polarization Magic Angle Spinning
$C$	gas concentration; concentration of diffusant
$C$	mass transfer in the stationary phase of a chromatographic column
$C_1$	high concentration side of diffusant through a sheet or membrane
$C_2$	low concentration side of diffusant through a sheet or membrane
$C_D$	gas concentration by normal dissolution
$C_H$	gas concentration by sorption in voidage areas of polymer
$C'_H$	total gas concentration by sorption in voidage areas of polymer at saturation
$C(t)$	solute concentration in the gas phase at time $t$
$C_s(x)$	diffusant concentration distribution in the steady state
$c_p^s$	concentration of the sorbate in the polymer
$cs$	recorder chart speed
DSC	Differential Scanning Calorimetry
$D$	diffusion coefficient
$D'$	average variable diffusion coefficient
$D_0$	diffusion coefficient as concentration approaches zero

$D_D$	diffusion coefficient for the Henry's law mode sorbed gas molecules
$D_H$	diffusion coefficient for the Langmuir mode sorbed gas molecules
$D_T$	thermodynamic diffusion coefficient of the diffusant component relative to the polymer component
$D_{T1}$	thermodynamic diffusion coefficient for Henry's law mode sorbed species
$D_{T2}$	thermodynamic diffusion coefficient for Langmuir mode sorbed species
$D_a$	diffusivity of a gas for a completely amorphous polymer
$D_g$	diffusion coefficient of the mobile phase
$D_p$	diffusion coefficient of the stationary phase
$dw/da_s$	slope of a sorption isotherm
$E_D$	activation energy of diffusion
$E_P$	activation energy of permeation
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
$F$	ratio of the diffusion coefficient of the Langmuir mode and Henry's law mode sorbed gases
$F$	rate of transfer of diffusant per unit area of section
$f$	measured carrier gas flow rate
GPC	Gel Permeation Chromatography
$\Delta G_S^0$	standard Gibbs free energy
$H$	plate height
$\Delta H_S$	partial molar enthalpy of sorption
$h$	chromatographic peak maximum
$ierfc$	initial error function
IGC	inverse gas chromatography
IUPAC	International Union of Pure and Applied Chemists
$J$	rate of transfer of diffusant per unit area of section
$K$	partition coefficient
$K_B$	bulk partition coefficient
$K_A$	surface partition coefficient
$K_d$	interfacial desorption rate coefficient

$k_D$	Henry's law of dissolution constant
$L$	chromatographic column length
$L'$	intercept on the $t$ -axis for time lag permeation model
$LCP$	liquid crystalline polymer
$l$	film or membrane thickness
$M$	mass of diffusant
$M_s$	molecular weight of molecular probe
$M_t$	mass of diffusant lost
$M_\infty$	mass of diffusant lost until equilibrium is achieved
$m_d$	mobility of the diffusant component relative to the polymer component
$m_p$	mass of the stationary phase
$m_s$	mass of an injected species
NMR	Nuclear Magnetic Resonance
$N$	Avogadro's number
$n$	number of moles
PEN	poly(ethylene naphthalate)
PET	poly(ethylene terephthalate)
$P$	permeability coefficient
$P_e$	environment pressure of surrounding room
$P_{in}$	chromatographic column inlet pressure
$P_{out}$	chromatographic column outlet pressure
$p$	applied pressure
$p$	volume percent of polymer in solution
$p_f$	upstream pressure imposed on a membrane
$p_p$	downstream pressure imposed on a membrane
$p_s$	equilibrium partial pressure of molecular probe
$p_s'$	standard adsorption state of molecular probe
$p_v$	sorbate partial vapor pressure
$p_s^v$	sorbate vapor pressure at saturation
$p_s'^v$	sorbate standard state vapor pressure as defined by De Boer
$p_s/p_s^v$	activity of sorbate

$Q_t$	amount of diffusant which passes through a sheet or membrane
$q$	rate of transfer of diffusant per unit area of section
$q'$	geometric packing factor of the stationary phase
$R$	universal gas constant
$R'$	chromatographic column inner radius
SEM	Scanning Electron Microscopy
$S$	solubility coefficient
$S'$	surface area of stationary phase in a chromatographic column
$S_a$	solubility coefficient for a pure amorphous polymer
TCD	thermal conductivity detector
TGA	thermogravimetric analysis system
$T$	absolute temperature of a system
$t$	time
$t_0$	retention time of a non-reacting species
$t_{1/2}$	time at which half of the equilibrium migrant has penetrated the sheet or membrane
$t_r$	retention time of molecular probe
$T_C$	chromatographic column temperature
$T_e$	environment temperature of surrounding room
$T_g$	glass transition temperature of a polymer
$T_m$	crystalline melt point of a polymer
$T_R$	room temperature
UHT	Ultra-high-temperature pasteurization
$\mu$	chemical potential of the penetrant species
$\mu$	carrier gas flow rate corrected to account for pressure drop along the chromatographic column
$\mu_1$	mean retention time (first statistical moment)
$\mu_2^*$	variance of chromatographic peak (second statistical moment)
$V_B$	volume of the stationary phase
$V_R$	retention volume
$v_f$	average fractional free volume of a system

$\alpha$	cross sectional area available for gas transport in a polymer matrix
$\beta$	activation energy required for gas diffusion through polymers
$\rho_p$	density of polymer
$\rho_s$	density of molecular probe
$\sigma^2$	statistical variance
$\theta'$	fraction of polymer voidage area occupied by any molecule at any instant
$\phi_a$	amorphous volume fraction
$\tau$	tortuosity factor accounting for the hindrance to the gas molecules due to the presence of the crystalline phase
$\tau$	film thickness
$\varepsilon$	ratio of the stationary-phase volume to the gas-phase volume
$\pi_s$	a measure of the reduction in the surface free energy of a solid as a result of the adsorption of a vapor at an equilibrium pressure $p_s$