This is to certify that the

thesis entitled

MODIFYING THE SORPTION CAPACITY OF POLYETHYLENE
FOR ORGANIC COMPOUNDS

presented by

Takashi Urata

has been accepted towards fulfillment
of the requirements for

Master degree in Packaging

Hernandez

Major professor

Date July 13, 1994

MODIFYING THE SORPTION CAPACITY OF POLYETHYLENE FOR ORGANIC COMPOUNDS

By

Takashi Urata

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1994

ABSTRACT

MODIFYING THE SORPTION CAPACITY OF POLYETHYLENE FOR ORGANIC COMPOUNDS

By

Takashi Urata

Several concentrations of sorbents (activated carbon and Tenax) blended polyethylene films were made to observe their sorption behavior against limonene, ethyl acetate, and toluene. A gravimetric method was used to determine the sorption characteristics of the films. In addition, density and selected mechanical properties of the sample were measured. To obtain a close look of the distribution of sorbents in the polymer's matrix, sample were observed under an optical microscope.

Activated carbon blended polyethylene films sorbed greater amounts of organic volatiles than polyethylene for all sorbates. Tenax blended polyethylene films showed good sorption behavior for ethyl acetate and toluene. However, very little sorption was observed for limonene.

From the sorption study of several types of polyethylene samples (granular, thin, and thick films), the sorption characteristics seemed to be concentration dependent. But that was not confirmed in this study.

Acknowledgements

I would like to express sincere thanks and appreciation to my major advisor, Dr. R. Hernandez, for his inspiration, counsel, and encouragement during the time spent at Michigan State University.

Appreciation is also extended to Drs. J. Giacin, J. Lucas, and P. Ng for serving as members of the guidance committee and for their very helpful comments and suggestions for the improvement of this thesis.

In addition, I would like to thank Mr. Mike Rich for his help and advice on extrusion process and optical observations at Composite Materials and Structures Center, Michigan State University.

Special thanks are expressed to Toppan Printing Co. Ltd., who made this graduate work possible, for their continued support.

Finally, I would like to express my appreciation to my family and all my friends for their help and encouragement.

Table of Contents

VII. Appendices

List of Tables

List of Figures

Nomenclature

a	activity of sorbent
b	experimental constant in reciprocal pressure units which has limited practical application (Equation 2)
B	penetrant driving force in units of concentration or pressure (Equation 5)
C	experimental constant (Equation 3)
$[Caq]_{eq}$	equilibrium concentration of aroma compound in aqueous solution (Equation 4)
$[Cp]_{eq}$	equilibrium concentration of aroma compound in plastic film (Equation 4)
C_s	concentration of sorbate in sample film
k	Boltzmann's constant
K_e	equilibrium partition coefficients
n	number of molecules striking each cm^2 of the surface every second (molecules/cm^2/sec) (Equation 1)
p	pressure of sorbent at test temperature
p_s	saturated pressure of sorbent at test temperature
M	molecular weight (Equation 1)
M_{PE}	weight of blended polyethylene (Equation 9)
M_S	weight of blended sorbent (Equation 9)
M_∞	total amount (mass) of vapor absorbed by the polymer at equilibrium for a given temperature (Equation 5)
N_1	number of molecules of solvent (Equation 7)

N_2	number of molecules of polymer (Equation 7)
S	sorption coefficient (kg/kg-Pa)
ΔS	entropy of mixing
S_{max}	maximum calculated sorption capacity (Equation 9)
S_{PE}	sorption coefficient of polyethylene (Equation 9)
S_S	sorption coefficient of sorbent (Equation 9)
T	absolute temperature (°K)
V	valves in Figure 2 (V1 ~ V9)
V_1	volume fraction of solvent (Equation 7)
V_2	volume fraction of polymer (Equation 7)
V_g	volume of gas adsorbed per unit mass of adsorbent (Equation 2)
V_m	volume of gas adsorbed per unit of adsorbent with a layer one molecule thick (Equation 2)
W	number of lattice in polymer matrix (Equation 6)
X	number of occupied sites in a lattice (Equation 7)
χ	interaction parameter (Equation 8)
ω	weight of the polymer sample (kg) (Equation 5)

Introduction

Nowadays, consumers want to have higher quality and safer food products. Given that, attention to the interaction between food products and packages is becoming more important. Keeping good environmental conditions inside of a product's package provides longer shelf life and better stability during storage of that product.

To modify the environment inside the package, several active packages have been developed (Labuza and Breene, 1989). An active package is one which can interact with a packed product or its environment to alter the in-package environment (Sacharow, 1991). An example of an active package is the sachet type oxygen absorber which has the inherent property of absorbing oxygen. Although this packaging method requires high barrier packaging materials and better seal integrity, it can extend the shelf life of the product considerably.

Limitations to shelf life are not only caused by oxygen, but also by many organic volatile substances. Such volatile substances may come from outside of the package. For example, they may come from the ink on the carton in which the product is packaged, or from the secondary package such as corrugated board container. The amount of these impurities may be very small, but may impart an off-flavor to the packaged product. Very small amounts of volatile, low molecular weight organic compounds can influence overall product flavor (Parliment, 1987).

In order to control or minimize this type of product/package interaction, at least two approaches are possible. One is the use for packaging of a high barrier polymer for which organic volatile substances have very low diffusion coefficient values. The other is the use of a polymer which has the barrier property of high capacity for retention of organic substances.

There is a need for the development of a material that has a higher sorption capacity than regular polymers. This may be accomplished by modifying a commercial polymer with a known compound which has high sorption properties such as Tenax or clays (Bigg, 1992). Additionally, these modified polymers could be used to as a flavor releaser. Flavor could be added to the sorbents before packing the product, allowing the sorbents to release the flavor slowly during storage. Therefore, even after opening, the product would keep good flavor longer than in a typical package.

The objective of this thesis was to explore the possibility of modifying a polymer to increase its sorption characteristics by blending an active sorbent compound with a polymer. Since the mechanical properties of the blended polymer can be affected by the concentration and distribution of an active sorbent compound, selected mechanical properties of the blended polymer were evaluated at several concentrations of active sorbent compounds.

Literature Review

1. Product/Package Interactions

Flavor and aroma characteristics arise from low molecular weight, volatile organic substances. These compounds are often present in food products at low concentrations, which influence the flavor profile of the foods (Parliament, 1987). Flavor causing compounds are known to be sorbed into packaging materials during their packaged period (Hotchkiss, 1988) and this is called scalping. Packaging polymers can sorb enough aroma compounds to be detected by human senses. Therefore, the package material often alters the flavor characteristics of a packaged food.

Other flavor changes can result from interactions with heat, light, or oxygen in the head space, or from chemical changes in the container (DeLassus et al., 1988).

Plastic containers have more complex flavor interactions than glass or metal. In addition to the factors of heat and light, plastic containers have three more concerns: (1) Molecules from the environment can permeate the package wall and enter the food. These molecules may be as simple as oxygen or as complex as the floral essence from the laundry products in the next aisle of the supermarket; (2) molecules that may come from the plastic itself, from a coating, or from an adhesive might migrate to the food; and (3) flavor molecules can leave the food by permeation into and through the plastic walls of the package.

Therefore, organic solvents and flavor and aroma molecules may contaminate food from several external sources such as printing inks or adhesives and cause flavor degradation (Strandburg et al., 1991). To minimize flavor losses many plastic food packages have a barrier layer in their structures. This barrier layer minimizes the entrance of flavor-degrading material from outside of the package (Hotchkiss, 1988). The barrier layer is made of high barrier polymers such as polyvinyl chloride (PVDC) copolymers, ethylene-vinyl alcohol (EVOH) copolymers, amorphous nylon polymers, silica coated polymer films, and high melt viscosity polyesters (Bigg, 1992). Flavor degradation from external materials can be reduced or eliminated by such barrier layers. Different techniques are required to reduce flavor loss from food into the packaging material.

The loss of flavor compounds due to sorption by plastic packaging materials can be considerable. The equilibrium uptake of volatile flavor compounds by plastic packaging materials may be on the order of several weight percent of the plastic. Because of sorption by the plastic packaging materials, the polymer layer in contact with the food may change the flavor of a food by selectively sorbing one or more compounds which influence the overall aromatic characteristic of that food. The specific compound which would be sorbed by the polymer may be a key flavor component, or one which combines with another to produce flavor of the food. For example, polymers such as polyolefins have been shown to selectively sorb flavor constituents (Foster, 1987). Orange juice develops a “flat”, non-fresh taste due to loss of volatile compounds that were sorbed by polymeric packaging materials (Marshall et al., 1985).

Migration of some component of food to the packaging materials which raises possible health concerns. Food processors generally claim that their suppliers provide letters of certification that their materials will not decrease quality of food as a result of unnecessary migration, or meet certain Food and Drug Administration (FDA) regulations (Bentley, 1988; Heckman, 1991). Low molecular substances migrating from plastic packaging materials in direct contact with the food are considered as indirect food additives by FDA (21 CFR 177.1010-.2000, 1993).

2. Sorption of Organic Compounds by Sorbents

The interaction at the interface between two phases involving the transition of a molecule from one phase to another and driven by different concentration values, can be considered as the sorption of the molecule (Kovach, 1978). From the viewpoint of the distribution of the substances to be sorbed, two types of sorption can happen: adsorption and absorption. Adsorption involves the accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases; liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. On the other hand, absorption is a process in which the molecules or atoms of one phase interpenetrate almost uniformly to the other phase to form a solution-like part with the second phase.

The phenomenological differences between adsorption and absorption are illustrated graphically in Figure 1 for reactions of each type in which a substance moves from liquid phase to solid phase (Weber, 1972). For adsorption, curves I and III indicate curvilinear dependence of the amount concentrated at the solid surface on the amount remaining in the solution phase for favorable and unfavorable separation patterns, respectively. Curve II represents a linear adsorption pattern. It also shows absorption which occurs in direct proportion to concentration. These graphs show the adsorption is described by a Langmuir type of isotherm, and the absorption is represented by Henry's Law. As stated above, absorption is a phenomena which the molecules or atoms of one phase interpenetrate almost uniformly to the other phase to form a solution-like part with the second phase. Therefore, the amount of substance moved across the interface and concentration of substance moves from liquid phase to solid phase show a linear relationship. Adsorption involves the accumulation or concentration of substances at a surface or interface. So its curve indicates curvilinear dependence

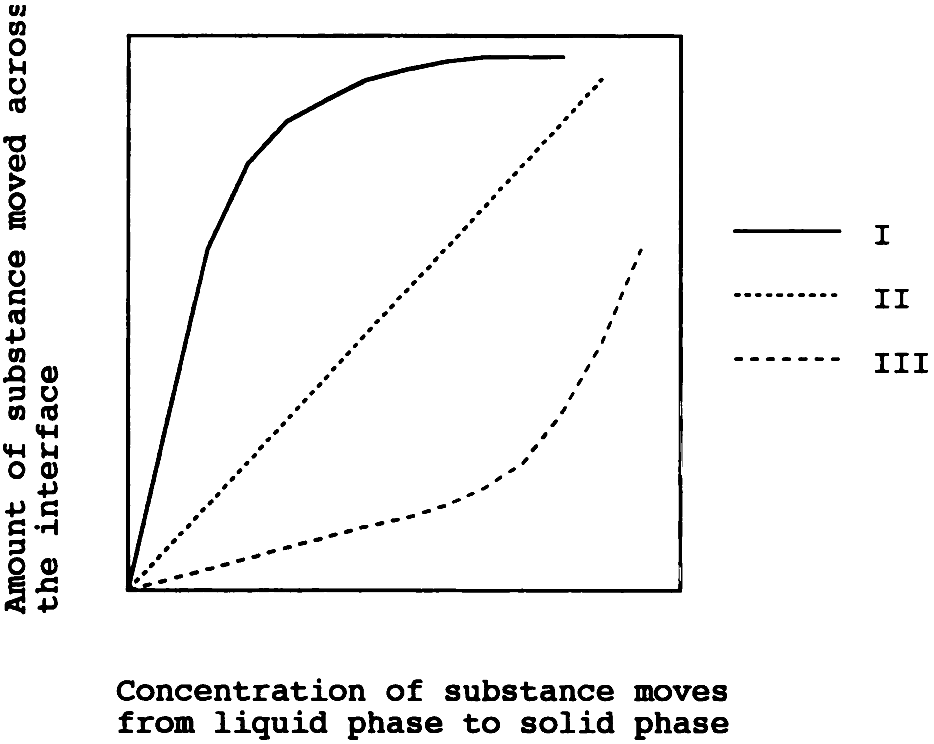


Figure 1. Types of sorption separations (Weber, 1972)

of the amount concentrated at the solid surface on the amount remaining in the solution phase.

There are two methods by which organic compounds may be adsorbed: physical and chemical adsorption (Cheremisinoff and Morresi, 1978). When physical adsorption occurs as a result of energy differences and/or electrical attractive forces, or weak van der Waals forces, the organic molecules become physically fastened to the adsorbent molecules. This type of adsorption may be multilayered: each molecular layer forms on top of the previous layer with the number of layers being proportional to the organic compound's concentration. More molecular layers form with higher concentrations of the organic compound.

When a chemical compound is produced by the reaction between the adsorbed organic molecule and the adsorbent, chemical adsorption has occurred. Unlike physical adsorption, this process is one molecule layer and quasi-irreversible. Because energy is required to form the new chemical compound at the surface of the adsorbent, energy would be necessary to reverse the process. The reversibility of physical adsorption is dependent on the strength of attractive forces between organic compound and the adsorbent. If these forces are weak, desorption is readily achieved.

Factors affecting adsorption include: (1) the physical and chemical characteristics of the adsorbent, e.g.: surface area, pore size, chemical composition, etc.; (2) the physical and chemical characteristics of the organic compound, e.g.:

molecular size, molecular polarity, chemical composition, etc.; (3) the concentration of the organic compound in the phase in contact with the adsorbent; (4) the characteristics of the phase in contact with the adsorbent, e.g.: pH, temperature, and (5) the residence time of the system.

Therefore, the diameter of pores and the surface area of adsorbents affect the capacity and characteristics of their adsorption. Table 1 presents some structural characteristics of activated carbon and Tenax.

Table 1. Some structural characteristics of activated carbon and Tenax

	Activated carbon	Tenax
Surface area (m^2/g)	500~2000[a]	18.6[c]
Average pore radius (Å)	23~30[b]	720[c]
Density (g/cm^3)	0.40~0.51[b]	0.37[c]

[a] Kovach, 1978.
[b] Darco, Atlas Chemical Div., ICI America, Inc., 1965
[c] Sakodynskii et al., 1974

In the case of the gas-phase adsorption, the number of volatile molecules present at the surface of adsorbent is dependent on the number that reach the surface and on the residence time of these molecules on the surface (Kovach, 1978). The number of volatile molecules that reach the surface of adsorbent is directly related to the speed of the molecules within the system. This number can be calculated using Maxwell's and Boyle-Gay Lussac's Equations.

$$n = 3.52 \times 10^{22} \times \frac{p}{\sqrt{MT}} \qquad (1)$$

where n = number of molecules striking each cm^2 of the surface every second

p = pressure of sorbent

M = molecular weight

T = absolute temperature

The Langmuir adsorption isotherm describes the adsorption behavior between the adsorbent and the gas phase of volatile compounds. The Equation of the Langmuir adsorption isotherm is shown as Equation 2.

$$V_g = \frac{V_m bp}{1 + bp} \qquad (2)$$

where V_g = volume of gas adsorbed per unit mass of adsorbent

V_m = volume of gas adsorbed per unit of adsorbent with a layer one molecule thick

b = experimental constant in reciprocal pressure units which has limited practical application

The Langmuir isotherm only describes monolayer adsorption of an adsorbent. For multilayer adsorption, the BET equation (Equation 3) can express the isotherm at the gas phase.

$$V = \frac{V_m Ca}{(1 - a)[1 + (C - 1)a]} \qquad (3)$$

where C = experimental constants

a = activity of sorbent

$$a = \frac{p}{p_s}$$

p_s = saturated pressure of absorbent at test temperature

2.1 Activated Carbon

The effectiveness of activated carbon for the removal of organic compounds by adsorption is enhanced by its large surface area, a critical factor in the adsorption process (Cheremisinoff and Morresi, 1978). This large surface area is provided by its pore structure. Since adsorption is possible only in those pores that can be entered by molecules, the carbon adsorption process is dependent on the physical characteristics of the activated carbon and the molecular size of the organic compound.

Of much less significance than its surface area is the chemical nature of the carbon's surface. This chemical nature or polarity varies with the carbon type and can influence attractive forces between molecules. Silica gel, an adsorptive media that is not a carbon compound, has a polar surface which also shows an adsorptive preference for unsaturated organic compounds as opposed to saturated compounds. However, for the most part activated carbon surfaces are nonpolar, making the adsorption of inorganic electrolytes difficult and the adsorption of organic compounds easy.

Cookson (1978) reported that aromatic rings of aromatic compounds act as electron acceptors, and carbonyl oxygens on the carbons are electron donors; this implies a donor-acceptor relationship. For non-polar aliphatic compounds, the oxides on the surface of activated carbon prohibit adsorption, and the metals on the activated carbon's surface allow it. To permit the adsorption of polar compounds, acidic oxides provide polar characteristics to activated carbon.

2.2 Tenax

Tenax is a 2,6-diphenyl-p-phenylene oxide based porous polymer column packing material (Van Wijk, 1970). It is suitable for the separation of high boiling polar compounds. This material is also used in adsorbent traps to collect organic compounds from air or gas (Patton et al., 1992; Sharp et al., 1992). For this use, the collection efficiencies of Tenax for low molecular weight, volatile compounds less than or equal to C_6 are often unacceptable for quantitative purposes (Heavner, 1992). Therefore, to collect volatile compounds in the air, "multisorbent" cartridges containing Tenax and other solid adsorbents are usually used.

The polarity of Tenax is relatively low, and its specific surface area is small (Daemen et al., 1975). These characteristics provide short retention times at low temperature for effective separation.

Vejrosta et al. (1988) reported the Langmuir adsorption isotherm was fit for benzene sorption on Tenax. This relationship was also applied to the sorption behavior of n-alkanes (Vejrosta et al., 1989).

2.3 Clay

The interaction between clay minerals and organic compounds has been a subject of research because this interaction raises the expectation that the adsorption of the organic fraction in the soil on the mineral particles would contribute to the physical stability of soil (Frissel, 1961).

The interactions between clays and organic substances, especially organic cation, have been studied extensively (Dixon and Weed, 1977; Mortland, 1970, 1986). The following factors may affect clay-organic cation interactions: (1) the properties of minerals, including cation exchange capacities, surface charge density, the cations on the exchange sites, the origin of charge, etc.; (2) the characteristics of organic cations, including molecular charge, lone pair electrons, polarity, molecular weight, etc.; and (3) the environments, including pH buffering, solution ionic strength, temperature, concentration of the organic cation, the presence of other cations, etc.

Many mechanisms for clay-organic interactions are discussed (Mortland, 1970, 1986), such as: (1) ion exchange: substitution of organic cations for hydrated metal cations on the mineral surface; (2) protonation: proton-donating and proton-accepting; (3) coordination and ion dipole: organic cations acting as ligands; (4) hydrogen bonding: relatively weak interactions between proton and electronegative elements; and (5) van der Waals forces: relatively weak physical interactions.

2.4 Plastic Packaging Materials

Many studies are done for sorption characteristics of organic materials by plastic packaging materials (Hirose et al., 1988; Imai, 1988; Schroeder, 1989).

Equilibrium partition coefficients (K_e) for sorption of aroma compounds by plastics packaging materials in an aqueous system were calculated by following equation (Kwapong and Hotchkiss, 1987).

$$K_e = \frac{[C_p]eq}{[C_{aq}]eq} \qquad (4)$$

where $[C_p]eq$: the equilibrium concentration of aroma compound in the plastic film

$[C_{aq}]eq$: the equilibrium concentration of aroma compound in the aqueous solution

The resulting K_e values were indicative of an aroma compound's strong affinity for plastic films, such as low density polyethylene, and ionomers. Although Equation 4 is based on an aqueous system, the partition coefficient would be able to apply between polymers and sorbents.

A sorption coefficient can be calculated from sorption experiments using the following equation:

$$S = \frac{M_\infty}{\omega B} \tag{5}$$

where S : sorption coefficient
M_∞ : total amount (mass) of vapor sorbed by the polymer at equilibrium for a given temperature
ω : weight of the polymer sample
B : penetrant driving force in units of concentration or pressure

Equation 5 can be applied to organic vapors exhibiting non-ideal diffusion, as well as non-interacting penetrants (Hernandez et al., 1986).

To explain the mixing of polymer solution, a two-dimensional lattice structure is used to represent non-polymer liquid (Billmeyer, 1984). Although the molecules of a pure component can be arranged in only one way on such a lattice, assuming that they cannot be distinguished from one another, the molecules of a mixture of two components can be arranged on a lattice in a large but calculable number of ways: W. By the Boltzmann's principle, the entropy of mixing is expressed as following:

$$\Delta S = k \ln(W) \tag{6}$$

where ΔS = entropy of mixing

k = Boltzmann's constant

It is assumed that the polymer molecules consist of a large number of chain segments of equal length, flexibly joined together. Each link occupies one lattice site. The solution is assumed to be concentrated enough that the occupied lattice sites are distributed at random rather than lying in well-separated regions with X occupied sites each. There are fewer ways in which the same number of lattice sites can be occupied by polymer segments: fixing one segment at a lattice point severely limits the number of sites available for the adjacent segment. To calculate W for such a model, the Flory-Huggins theory of polymer solutions are used (Flory, 1953). The equation is as follows:

$$\Delta S = -k(N_1 \ln(V_1) + N_2 \ln(V_2)) \tag{7}$$

where N_1 = number of molecules of solvent

N_2 = number of molecules of polymer

V_1 and V_2 = volume fractions defined as:

$$V_1 = \frac{N_1}{N_1 + XN_2}$$

$$V_2 = \frac{XN_2}{N_1 + XN_2}$$

where X = number of occupied sites in a lattice

The entropy of mixing of each component can be represented by the volume fraction of the other component in diluted solutions (Huggins, 1942). For high molecular weight polymers, the Flory-Huggins expression is shown as Equation 8.

$$\ln (a) = \ln (V_1) + V_2 + \chi V_2{}^2 \tag{8}$$

where χ = interaction parameter

3. Analytical Method of Determining Sorption Capacity

The Electrobalance Sorption/Desorption Apparatus (Cahn Instruments Inc., Cerritos, CA) has been used in sorption studies of volatile flavor components (Mohney, 1988; Roland and Hotchkiss, 1991). In this apparatus, a test sample film is hung in the hangdown tube of an electrobalance and a gas-phase vapor generating/dilution system is used to get constant vapor concentration. A constant concentration of penetrant vapor stream is produced by bubbling nitrogen through liquid penetrant and dilution with untreated nitrogen, then passing it over the polymer. The polymer is continuously weighed by the electrobalance.

This method can be used to accurately measure flavor sorption by plastic materials which have been surrounded with a constant concentration of organic vapor. A limitation is that it can analyze only one component or set of components at a time. The minimum weight to detected by the electrobalance is 1/10 μg.

Materials and methods

1. Sorbent Blended with Polyethylene

Table 2 shows samples which were used to determine the density of them. The procedure to make these samples are described in appendix A.

Table 2. Samples used to determine density

Type of resin	concentration of sorbent (wt %)
polyethylene	0
activated carbon blended polyethylene	0.135
	1
	5
Tenax blended polyethylene	1.6
	2.8
	3.9

Table 3 shows samples which were used to determine the mechanical properties and sorption characteristics of them. The procedure to make these samples are described in appendix B.

Table 3. Samples used to determine mechanical properties and sorption characteristics

Type of film	concentration of sorbent (wt %)
polyethylene	0
activated carbon blended polyethylene	0.135
	1
	5
Tenax blended polyethylene	1.6
	2.8
	3.9

2. Determination of Density

Several polyethylene samples were blended with the indicated sorbents. The blended concentration was different for every sample. Therefore the density of these samples varied with type of blended sorbent and its concentration. To understand the relationship between density and sorbent, the density of each sample was measured.

The procedure was based on ASTM D 1505-85.

A density gradient column (Cole-Parmer Instrument Co., Chicago, IL) was prepared using isopropanol and water. The density range of this system is from 0.79 to 1.00 g/cm^3. Distilled water and 2-propanol (100 %, J.T.Baker Inc., Phillipsburg, NJ) was used.

Three standard glass beads (0.9282, 0.9342, and 0.9516 g/cm^3) were used to make the calibration curve for density of samples.

After the column was filled with the gradient mixture, the three standard glass beads were put into the column. After their sinking stabilized, the height of each of the standard floats from the bottom of the column was measured by a ruler. From these data, density versus height was plotted. The plot was used as a calibration curve to determine the density of samples. The calibration curve was made separately for Tenax and activated carbon.

All the samples were put into the same column as the standard glass beads, and their height from the bottom of the column were measured. Using the calibration curve, the density of each sample was determined with an approximation of ±0.001 g/cm^3 for activated carbon and ±0.011 g/cm^3 for Tenax, respectively.

3. Determination of Mechanical Properties

Several polyethylene samples were blended with the indicated sorbents. The blended concentration was different for every sample. Therefore the mechanical properties of these samples varied with type of blended sorbent and its concentration. To understand the relationship between mechanical properties and sorbent, tensile strength, %

elongation of at break, and elastic modulus of each sample was measured.

The procedure was based on ASTM D 882.

Sample films were cut by a JDC Precision sample cutter (model JDC25, Thwing-Albert Instrument Co., Philadelphia, PA) to get proper size for testing. The thickness of all specimens was measured by a micrometer (model 549, Testing Machines Inc., Amityville, NY) before the test. The specimen was placed in the grip of the Instron machine (model 4201, Instron Corporation, Liviona, MI), and the machine was started.

The testing conditions were as follows:

Width of specimen: 1 inch
Grip separation: 2 inches
Crosshead speed: 20 in/min.

The result was charted, and stress, strain, and modulus of elasticity were calculated for each specimen.

4. Optical Microscope Observation of Sample Films

It is extremely difficult to observe the distribution of sorbent in a film by the naked eye. In particular, observation of the cross sectional distribution of sorbent in a film is almost impossible. To know the distribution condition of sorbent is important to understand the sorption characteristics of the sorbent blended sample films. Such observations may help to explain the interactions between polyethylene and sorbent. Optical observation can provide magnified images of film samples, so it would be helpful in understanding the interactions between polyethylene and sorbent.

Each sample film was cut about 1 cm x 3 cm. To cut samples, a razor blade was used to obtain sharp edges. A small piece of sample film was put on a slide glass and set on the optical microscope (model BHS, Olympus Optical Co., Ltd., Tokyo, Japan). First, the sample film was focused at a low magnification (x100), then the magnification was changed to the desired setting. An automatic photomicrographic system (model PM-10ADS, Olympus Optical Co., Ltd., Tokyo, Japan) was attached to the microscope and magnified images of the sample film were taken at the desired magnification. The exposure time was automatically determined by this system.

This optical microscope system is available at the Composite Materials and Structures Center, Michigan State University.

5. Determination of Sorption Characteristics by Gravimetric Method

Theoretically, given sorbent sorbs sorbate up to its capacity. Therefore, it can be expected that the more sorbate sorbed into a sample film, the greater the weight of the tested sample. The gravimetric method is based on this expectation. The degree of sorption of each sorbate was determined by the weight change of the sample. This system requires a very sensitive balance to detect the weight change of samples

The schematic diagram of the electrobalance system (Cahn Instruments Electrobalance model 2000, Cahn Instruments, Cerritos, CA) is shown as Figure 2.

(R)-(+)-limonene, toluene, and ethyl acetate were studied as sorbates in this study.

Nitrogen gas was used as the carrier gas for the Electrobalance system.

The degree of absorption of each sorbate was determined by the weight change of the sample. To measure the absorption of the samples, the following techniques were applied:

1. The system was purged by nitrogen gas overnight to eliminate sorbate residues. In this phase, valve No.7 (V7) was closed, three-way valve No.9 (V9) was turned to waste, and valve No.1 (V1) and valve No.8 (V8) were opened.

2. For a film sample, the film was cut about 1 cm x 2 cm and weighed precisely by a Mettler AE-160 balance (Mettler Instrument, Hightstown, NJ). After weighing of sample, it was hung in the hangdown tube of the electrobalance and left until the balance stabilized.

For a granular sample, the sample was put on a small aluminum pan and weighed using the same method used for a

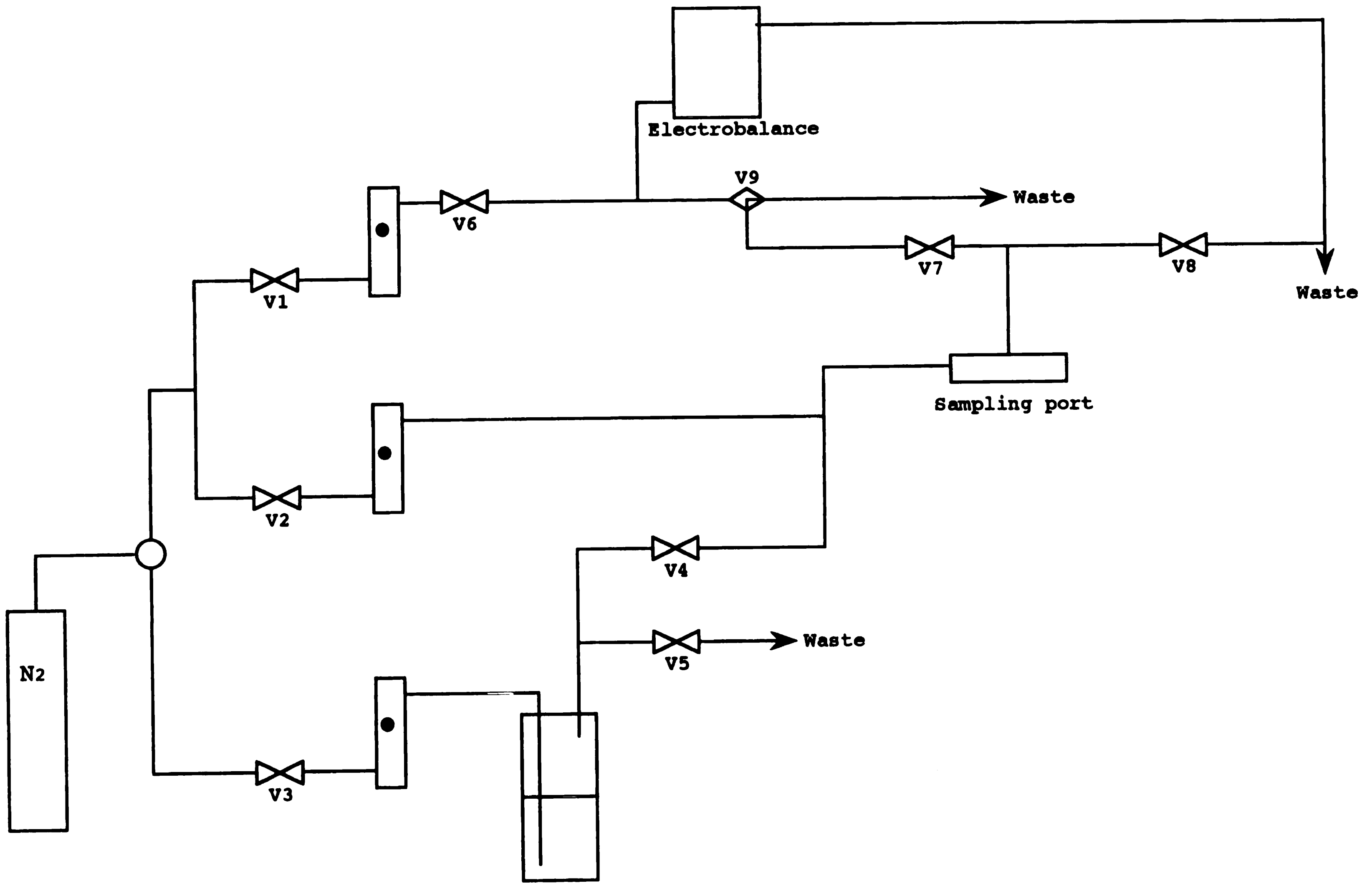


Figure 2. Schematic diagram of electrobalance system

film sample. Then the aluminum pan was hung in the hangdown tube of the electrobalance with a stirrup and left until the balance stabilized.

3. During the stabilizing of the balance, valves No.2 (V2), No.3 (V3) and No.4 (V4) were opened, and valve No.5 (V5) was closed to adjust the concentration of sorbate. 500 μl of sample used to determine the concentration of sorbate was obtained from the sampling port using a Gastight® #1750 syringe (Hamilton Co., NV), and directly injected into the gas chromatograph (Hewlett Packard HP5890A with flame ionization detector, Hewlett-Packard, Avondale, PA). The analyzing conditions of the gas chromatograph were set as shown in appendix C.

The concentration of sorbate was determined by the responded area units and calibration curve of each sorbate.

4. After stabilization of the sample, V6 and V8 were closed, V7 was opened, and V9 was turned to electrobalance to allow the carrier gas with sorbate to pass into the hangdown tube of the Electrobalance. The weight change of the sample was recorded by a recorder.

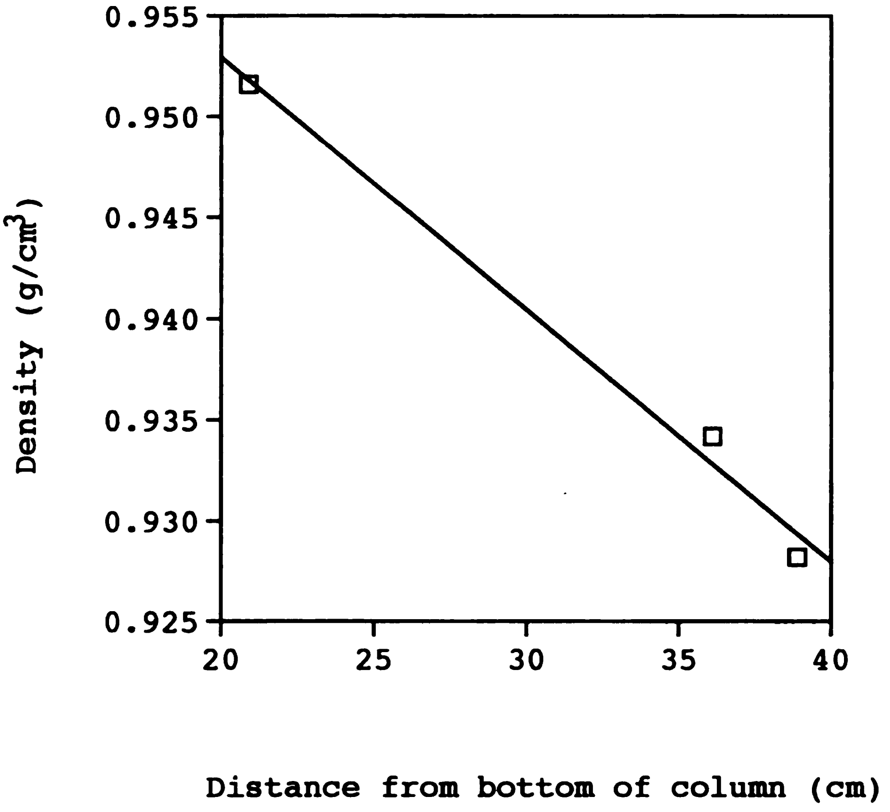
5. When the weight change reached equilibrium, the recorder was stopped; V7 was closed, V9 was turned to waste, V6 and V8 were opened to purge the inside of the hangdown tube.

Results and Discussion

1. Density of Samples

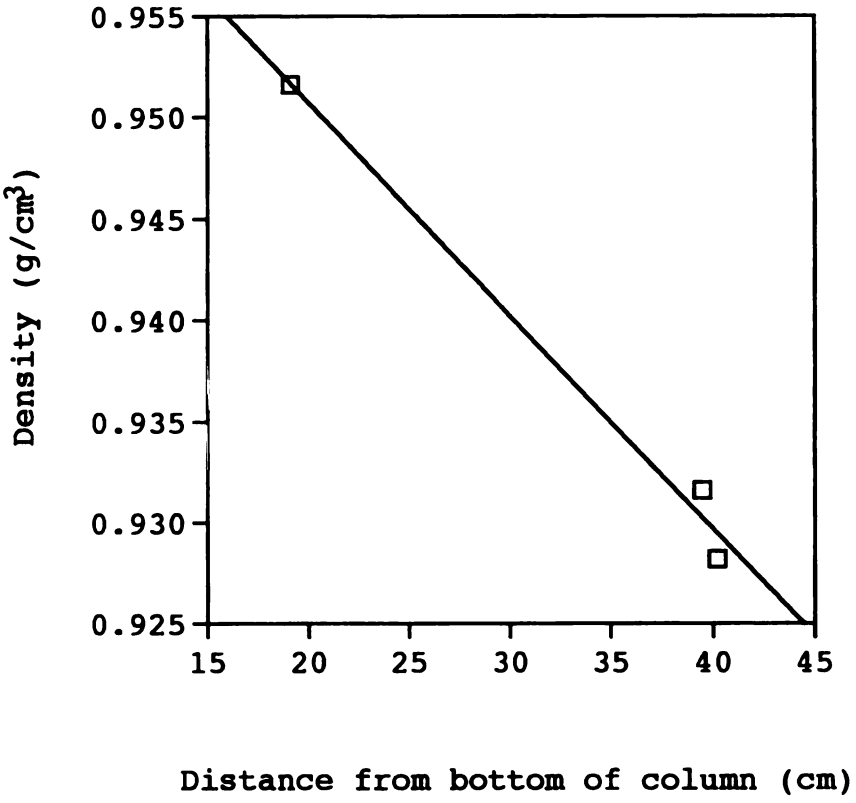
The calibration curves of density for activated carbon and Tenax are presented as Figure 3 and 4, respectively. The density of both samples was calculated using these calibration curves, and are shown in Table 4 and 5. From both Table 4 and 5, the concentration of sorbent versus density for each sorbent were plotted in Figures 5 and 6, respectively.

In Figures 5 and 6, both activated carbon and Tenax show a linear relationship between concentration of sorbent and density. Comparing these two results, Tenax showed a larger decrease in density than activated carbon; even the blended amount of Tenax is lower than that of activated carbon. This is caused by the density difference of these two sorbents. Table 1 shows that Tenax is lighter than activated carbon because of their relative densities (activated carbon: 0.40~0.51 g/cm^3; Tenax: 0.37 g/cm^3). Therefore, it required less Tenax than activated carbon to affect a given density of blended polymer.



$Y = -1.248 \times 10^{-3} X + 9.779 \times 10^{-1}$
$r^2 = 0.989$

Figure 3. Calibration curve for density of activated carbon blended samples



$Y = -1.05\times10^{-3}X + 9.72\times10^{-1}$
$r^2 = 0.989$

Figure 4. Calibration curve for density of Tenax samples

Table 4. Density of activated carbon blended samples

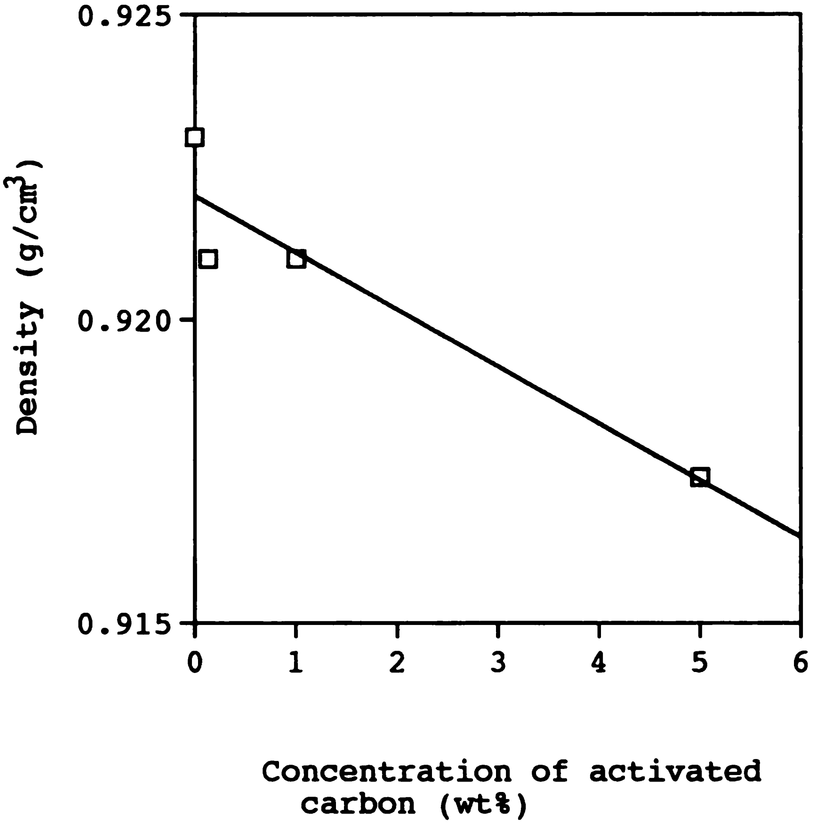
Concentration of activated carbon (%)	Density* (g/cm^3)
0	0.9230
0.135	0.9210
1	0.9210
5	0.9174

* The values were averages of replicated measurements.
Approximation: ±0.001 g/cm^3

Table 5. Density of Tenax blended samples

Concentration of Tenax (%)	Density* (g/cm^3)
0	0.9266
1.6	0.9242
2.8	0.9161
3.9	0.9008

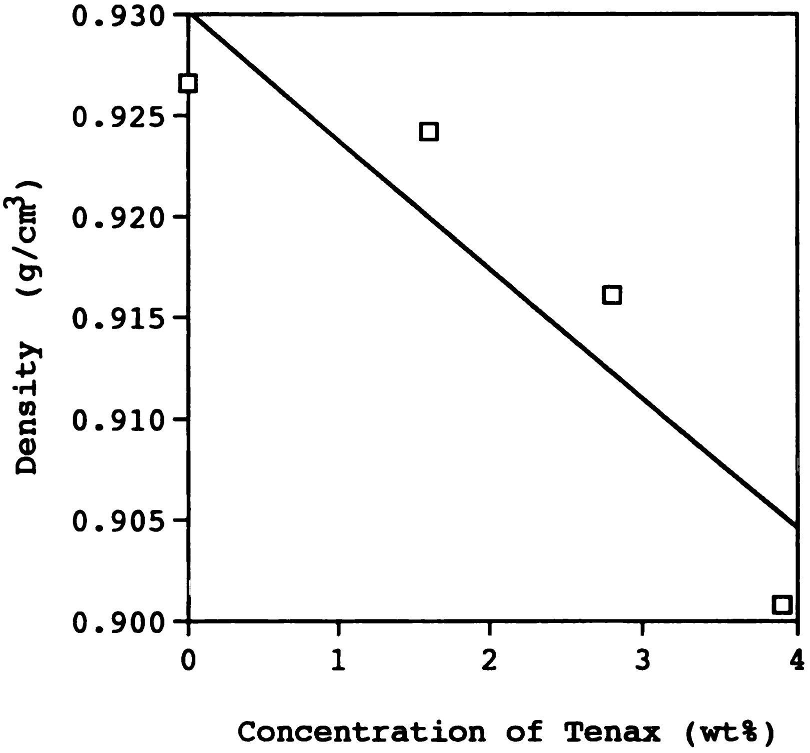
* The values were averages of replicated measurements.
Approximation: ±0.011 g/cm^3



$Y = -9.36 \times 10^{-4} X + 9.22 \times 10^{-1}$

$r^2 = 0.892$

Figure 5. Relationship between density and concentration of activated carbon



$Y = -6.39 \times 10^{-3} X + 9.30 \times 10^{-1}$
$r^2 = 0.840$

Figure 6. Relationship between density and concentration of Tenax

2. Mechanical Properties

Results of thickness, tensile strength, % elongation at break, and elastic modulus of each sample film are presented on Table 6. The values are averages of replicated measurements.

From those results, the elastic modulus versus the concentration of sorbents for both sample films is plotted in Figures 7 and 8, respectively. In addition, tensile strength and % elongation at break versus concentration of sorbents is presented in Figure 9 and 10, respectively.

It was observed that the greater the concentration of blended sorbents, the worse the mechanical properties of both materials. However, the degree of decrease in those properties varied.

It appears that a linear relationship between concentration of Tenax and elastic modulus is observed over the sorbent concentration levels investigated (Figure 8). On the other hand, a logarithmic relationship is shown for activated carbon over the blending concentration levels studied (Figure 7). The activated carbon drastically decreases the flexibility of polyethylene film, even at a loading level of 0.135 wt%. The degree of decrease approached equilibrium when 5 wt% of activated carbon was added. By contrast, Tenax reduced flexibility relatively slowly, but lost flexibility did not reach equilibrium even after 3.9 wt% of Tenax was blended. This phenomena may be related to differences in the size of the sorbent particles. From the optical microscope observation (Figures 11 and 12), the particle size of activated carbon is smaller than that of Tenax (activated carbon: 2.2 mm; Tenax: 3.1 mm). Therefore, Tenax blended polyethylene could lose its flexibility easier than activated carbon blended samples. This tendency can be seen graphically in Figures 9 and 10. As shown in Figure 10, the slope of losing elongation was sharper for Tenax than for activated carbon. The same effect was observed with decreasing elastic modulus.

Table 6. Mechanical properties of sample films

	thickness (mil)	tensile strength (psi)	% elongation at break (%)	elastic modulus (psi)
LDPE	3.64	1795.23	123.18	27738.03
LDPE*		1200~4550	100~650	25000~41000
Carbon blended LDPE				
0.135 %	4.38	1655.53	123.15	19821.55
1 %	4.17	1631.05	122.50	18211.68
5 %	4.21	1558.40	121.33	14646.70
Tenax blended LDPE				
1.6 %	3.59	1758.43	120.30	23238.08
2.8 %	3.60	1692.38	119.75	17977.65
3.9 %	3.71	1543.82	115.40	17508.47

*Data from Modern Plastic Encyclopedia (1990)

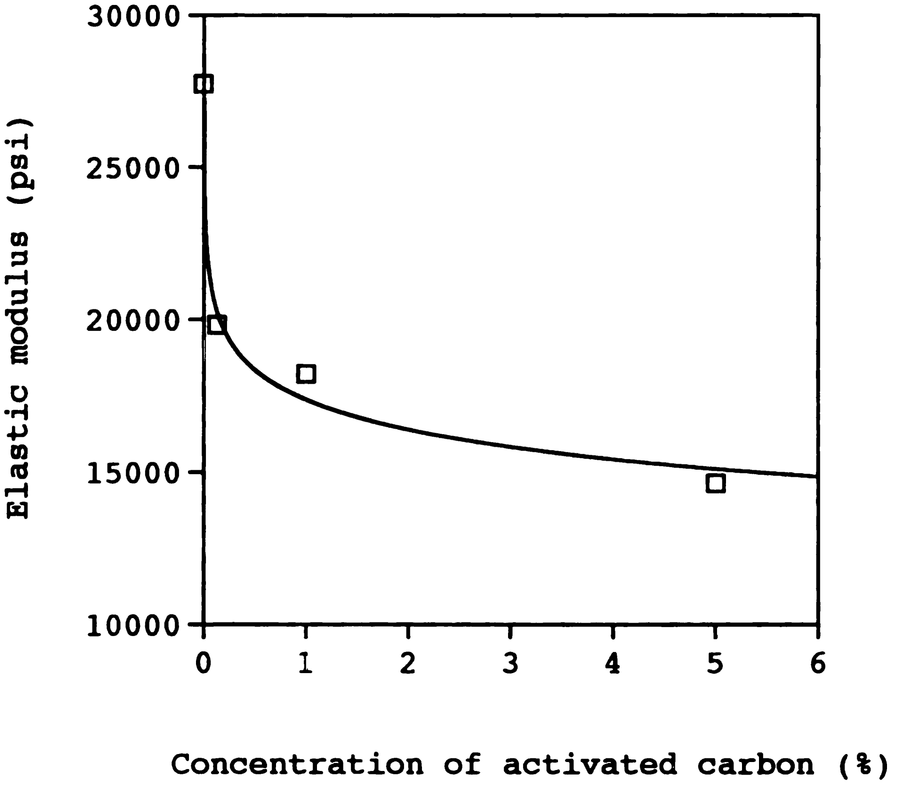


Figure 7. Relationship between concentration of activated carbon and elastic modulus

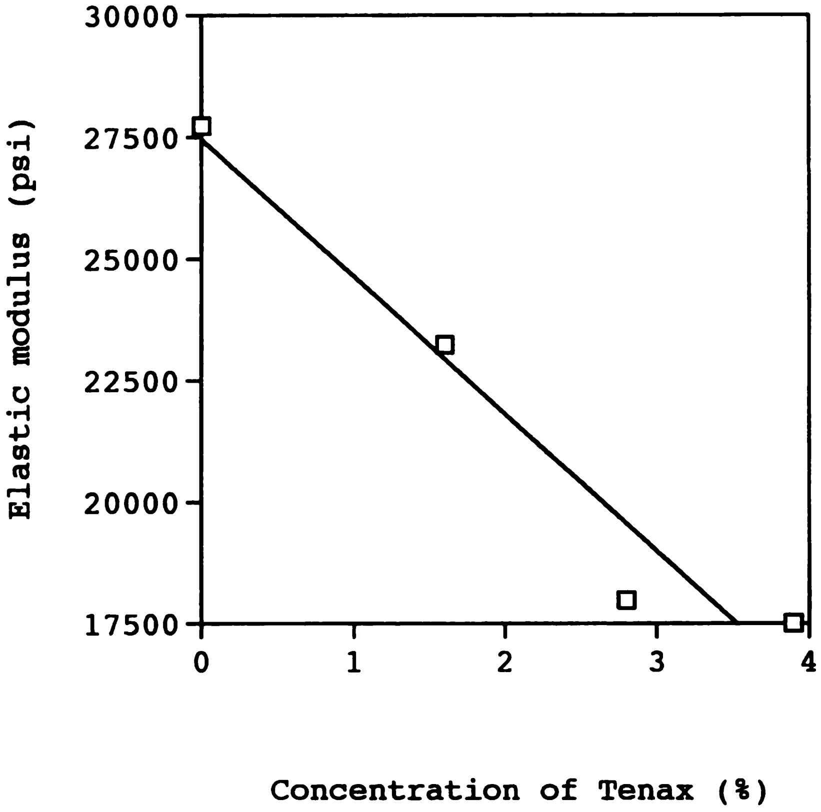


Figure 8. Relationship between concentration of Tenax and elastic modulus

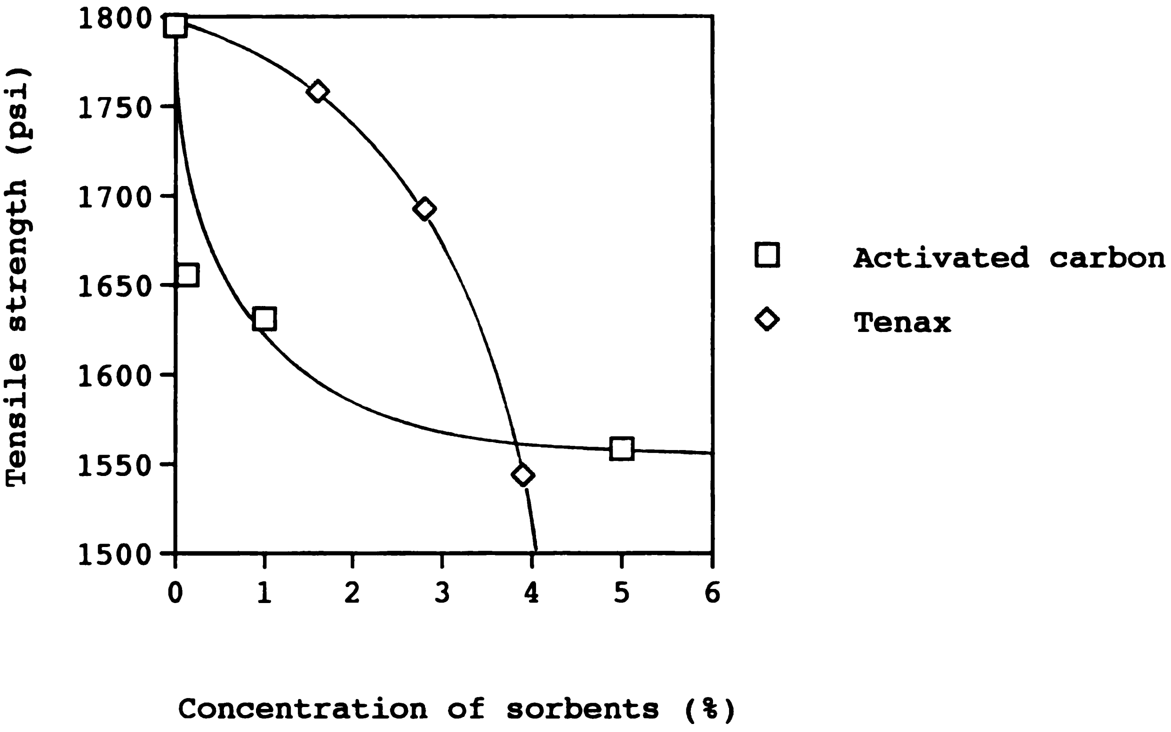


Figure 9. Relationship between concentration of sorbent and tensile strength

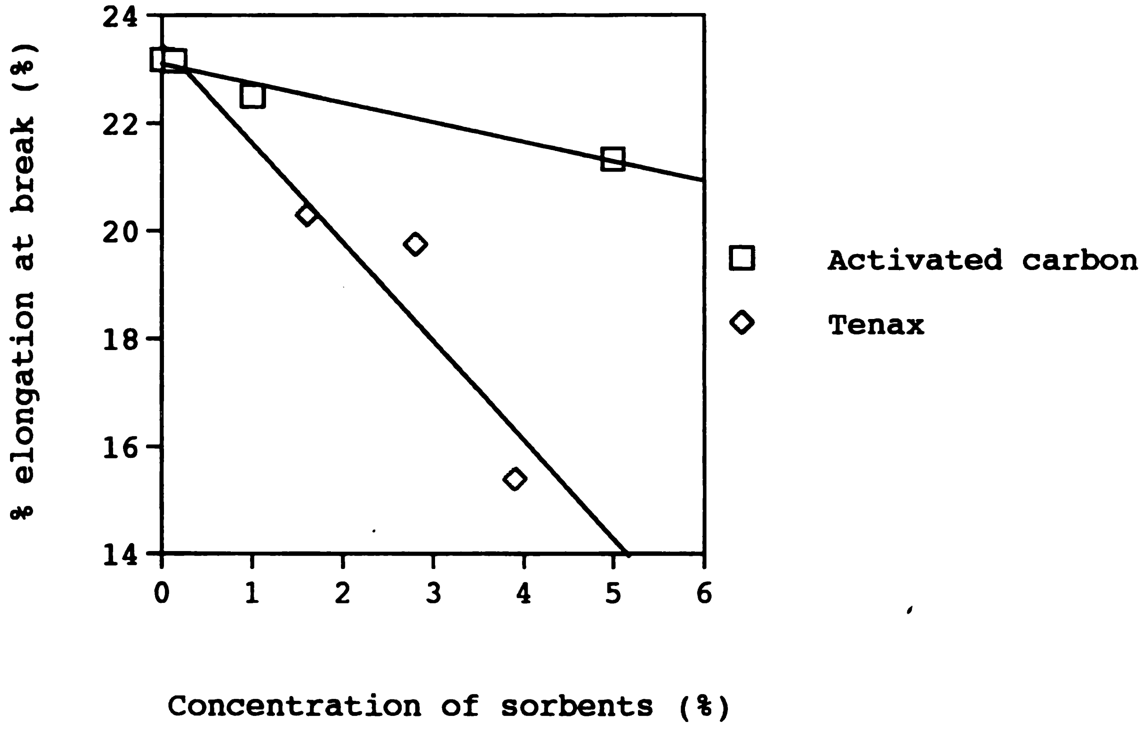


Figure 10. Relationship between concentration of sorbent and % elongation at break

3. Optical Microscope Observation of Sample Films

The results of optical observation are shown as Figures 11 ~ 20.

Figures 11 and 12 show a particle of activated carbon and Tenax, respectively. For these two figures, the magnification of microscope was x200. In these figures, it can be seen the different diameter and surface structure between the two sorbents.

Figure 13 shows the distribution of activated carbon particles in a 5 wt% concentration of sample film. The distribution and concentration of activated carbon appear to be random.

Figures 14 exhibits the distribution of Tenax particles in a 3.9 wt% concentration of sample film. As with activated carbon film sample, it suggests random distribution of Tenax. In addition, Tenax particle size is bigger than that of activated carbon. It mirrors the results shown in Figures 11 and 12.

The cross sectional view of polyethylene film is shown in Figure 15, which can be compared to Figures 16 and 17 presenting a cross sectional view of each blended sorbent. These figures present the condition of both sorbents in the thickness of the sample films. As shown in Figure 17, some particles of sorbent are completely surrounded in polyethylene.

To confirm these results, cross sectional pictures at the highest magnification (x1000) were taken as shown in Figures 18 ~ 20. They also show most of sorbent particles are surrounded in polyethylene.

There is less destruction of physical structure of Tenax than expected because the average diameter of Tenax is almost twice that of the thickness of the sample film. Therefore, the destruction of the porous structure of sorbent by making sample film would not affect the sorption characteristic of the sample film. The surface conditions of the sorbent which is buried in polyethylene cannot be confirmed from these pictures. Consequently, it would be difficult to say whether or not polyethylene surrounding sorbents interrupts sorption from these observations.

However, it appears that there is a good contact between the surface of the sorbent and polyethylene. This means no air gap appears to exist between the discontinuous and matrix phases. This is important because the uptake of the sorbate by the sorbent has to be made through the diffusion of the sorbate though the polyethylene matrix.

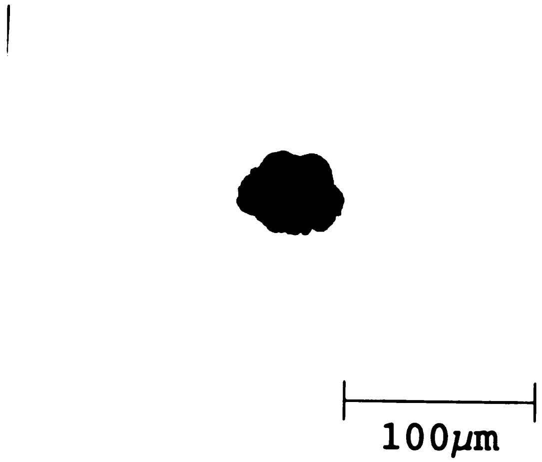


Figure 11. A particle of activated carbon (x200)

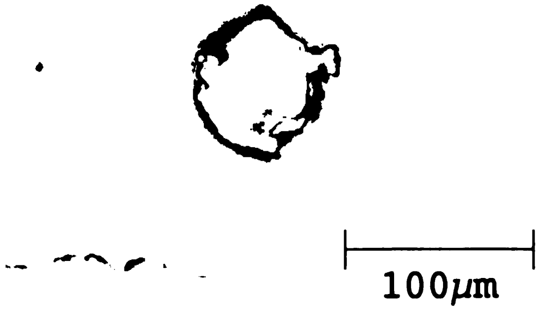


Figure 12. A particle of Tenax (x200)

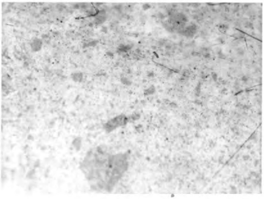


Figure 13. Surface of activated carbon blended film (5 wt%, x200)

Figure 14. Surface of Tenax blended film (3.9 wt%, x100)

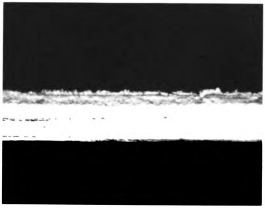


Figure 15. Cross sectional view of polyethylene film (x400)

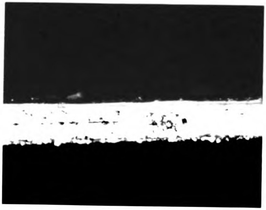


Figure 16. Cross sectional view of activated carbon blended film (5 wt%, x400)

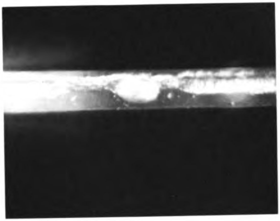


Figure 17. Cross sectional view of Tenax blended film (3.9 wt%, x400)

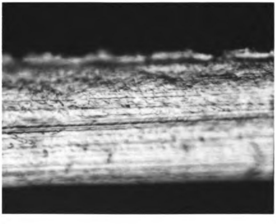


Figure 18. Cross sectional view of polyethylene film (x1000)

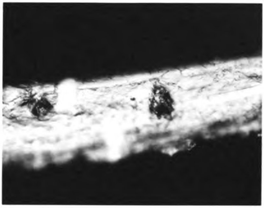


Figure 19. Cross sectional view of activated carbon blended film (5 wt%, x1000)

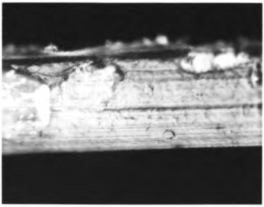


Figure 20. Cross sectional view of Tenax blended film (3.9 wt%, x1000)

4. Sorption Characteristics by Gravimetric Method

For this sorption study, the activity of sorbent was adjusted to 0.02 and 0.05. Table 7 shows the concentration in ppm (v/v) of each organic vapor at a = 0.02 and 0.05. The saturated vapor pressure was calculated based on the data reported by Perry et al. (1984).

Table 7. Concentration in ppm (v/v) of each sorbate for each vapor activity

vapor activity	0.02	0.05
limonene	0.35	0.70
ethyl acetate	9.59	19.19
toluene	2.71	5.41

Tables 8 ~ 10 show the results of sorption tests for each sorbent. In addition, the sorption characteristic of limonene was observed for granular, thin film and thick film polyethylene. The results are presented as Table 11. In these tables, C_s represents sorbate concentration (wt%) in the sample film, A/g stands for surface area of sample per unit mass (mm^2/g), and S is the sorption coefficient (kg/kg-Pa). It can be seen from these tables that for polyethylene the solubility of limonene is almost three order of magnitude larger than for ethyl acetate and two order larger than

Table 8. Results of sorption test for limonene

Type of samples	Thickness (mil)	Initial weight(g)	Increased weight(mg)	C_s (mg/g)	Vapor activity	S (kg/kg-Pa)
granular samples						
polyethylene		0.0358	0.1318	3.68	0.016	5.7×10^{-4}
		0.0073	0.0593	8.12	0.038	7.3×10^{-4}
activated carbon		0.0063	1.3337	211.70	0.015	4.7×10^{-2}
		0.0061	1.3338	218.66	0.037	2.0×10^{-2}
Tenax		0.0050	0.0780	15.60	0.022	3.2×10^{-3}
		0.0032	0.0559	17.47	0.035	1.7×10^{-3}
film samples						
polyethylene	3.6	0.0412	0.1505	3.65	0.022	5.7×10^{-4}
	3.6	0.0297	0.4162	14.01	0.047	1.0×10^{-3}
activated carbon						
0.135%	4.4	0.0513	0.2004	3.91	0.019	7.0×10^{-4}
	4.4	0.0329	0.4444	13.51	0.043	1.1×10^{-3}
1%	4.2	0.0921	0.4011	4.36	0.021	6.9×10^{-4}
	4.2	0.0338	0.4436	13.12	0.039	1.1×10^{-3}
5%	4.2	0.0472	0.1857	3.93	0.016	8.1×10^{-4}
	4.2	0.0346	0.4320	12.49	0.037	1.1×10^{-3}
Tenax						
3.9%	3.7	0.0356	0.1109	3.12	0.019	5.6×10^{-4}
	3.7	0.0250	0.3148	12.59	0.041	1.0×10^{-3}

C_s: Sorbate concentration in the sample film

S: Sorption coefficient

Table 9. Results of sorption test for ethyl acetate

Type of samples	Thickness (mil)	Initial weight(g)	Increased weight(mg)	C_s (mg/g)	Vapor activity	S (kg/kg-Pa)
granular samples						
polyethylene		0.0091	0.0004	0.04	0.022	$1.9\text{x}10^{-7}$
		0.0089	0.0004	0.04	0.050	$8.3\text{x}10^{-8}$
activated carbon		0.0058	0.1168	20.14	0.024	$7.7\text{x}10^{-5}$
		0.0085	0.1872	22.02	0.049	$4.2\text{x}10^{-5}$
Tenax		0.0048	0.0090	1.88	0.022	$7.9\text{x}10^{-6}$
		0.0043	0.0100	2.33	0.047	$4.6\text{x}10^{-6}$
film samples						
polyethylene	3.6	0.0384	0.0020	0.05	0.021	$2.3\text{x}10^{-7}$
	3.6	0.0445	0.0008	0.02	0.048	$3.5\text{x}10^{-7}$
activated carbon						
0.135%	4.4	0.0392	0.0032	0.08	0.024	$3.1\text{x}10^{-7}$
	4.4	0.0089	0.0008	0.09	0.048	$3.6\text{x}10^{-7}$
1%	4.2	0.0250	0.0024	0.10	0.025	$3.6\text{x}10^{-7}$
	4.2	0.0349	0.0076	0.22	0.050	$4.1\text{x}10^{-7}$
5%	4.2	0.0365	0.0026	0.07	0.024	$3.8\text{x}10^{-7}$
	4.2	0.0359	0.0080	0.22	0.048	$4.3\text{x}10^{-7}$
Tenax						
3.9%	3.7	0.0523	0.0060	0.11	0.023	$4.7\text{x}10^{-7}$
	3.7	0.0523	0.0080	0.15	0.049	$5.2\text{x}10^{-7}$

C_s: Sorbate concentration in the sample film
S: Sorption coefficient

Table 10. Results of sorption test for toluene

Type of samples	Thickness (mil)	Initial weight(g)	Increased weight(mg)	C_s (mg/g)	Vapor activity	S (kg/kg-Pa)
granular samples						
polyethylene		0.0067	0.0008	0.12	0.021	1.7×10^{-6}
		0.0077	0.0080	1.04	0.043	7.2×10^{-6}
activated carbon		0.0042	0.0956	22.76	0.021	3.3×10^{-4}
		0.0109	0.2560	23.49	0.044	1.6×10^{-4}
Tenax		0.0041	0.0088	2.15	0.022	3.0×10^{-5}
		0.0061	0.0224	3.67	0.044	2.4×10^{-5}
film samples						
polyethylene	3.6	0.0213	0.0128	0.60	0.023	7.8×10^{-6}
	3.6	0.0289	0.0384	1.33	0.045	8.7×10^{-6}
activated carbon						
0.135%	4.4	0.0382	0.0208	0.54	0.020	7.9×10^{-6}
	4.4	0.0306	0.0414	1.35	0.045	8.8×10^{-6}
1%	4.2	0.0199	0.0120	0.60	0.023	7.9×10^{-6}
	4.2	0.0329	0.0460	1.40	0.045	9.1×10^{-6}
5%	4.2	0.0234	0.0146	0.62	0.023	7.9×10^{-6}
	4.2	0.0265	0.0360	1.36	0.042	9.6×10^{-6}
Tenax						
3.9%	3.7	0.0316	0.0200	0.63	0.021	9.1×10^{-6}
	3.7	0.0290	0.0476	1.64	0.052	9.3×10^{-6}

C_s: Sorbate concentration in the sample film

S: Sorption coefficient

Table 11. Results of sorption test of several types of polyethylene samples for limonene

Type of samples	Thickness (mil)	Initial weight(g)	Increased weight(mg)	Vapor activity	A/g (mm^2/g)	S (kg/kg-Pa)
granular samples						
polyethylene		0.0358	0.1318	0.02	7692.7	5.7×10^{-4}
		0.0073	0.0593	0.05	4438.4	7.3×10^{-4}
film samples						
polyethylene	3.6	0.0412	0.1505	0.02	18966.0	5.7×10^{-4}
	3.6	0.0297	0.4162	0.05	17993.3	1.0×10^{-3}
	9.5	0.0629	0.4226	0.02	9316.4	1.1×10^{-3}

A/g: Surface area of sample per unit mass
S: Sorption coefficient

toluene. A similar relation exists for Tenax and activated carbon. Limonene, ethyl acetate and toluene sorbed better by activated carbon alone than by Tenax alone.

A maximum calculated sorption capacity (S_{max}) is described by Equation 9:

$$S_{max} = M_{PE}S_{PE} + M_{S}S_{S} \qquad (9)$$

where M_{PE} = weight of blended polyethylene

S_{PE} = sorption coefficient of polyethylene

M_S = weight of blended sorbent

S_S = sorption coefficient of sorbent

Tables 12, 13, and 14 show maximum calculated sorption capacity for limonene, ethyl acetate, and toluene, respectively.

Table 12. Maximum calculated sorption capacity for limonene

vapor activity	0.02	0.05
polyethylene	$5.7x10^{-4}$	$7.3x10^{-4}$
activated carbon blended		
0.135%	$6.3x10^{-4}$	$7.6x10^{-4}$
1%	$1.0x10^{-3}$	$9.2x10^{-4}$
5%	$2.9x10^{-3}$	$1.7x10^{-3}$
Tenax blended		
3.9%	$6.7x10^{-4}$	$7.7x10^{-4}$

Table 13. Maximum calculated sorption capacity for ethyl acetate

vapor activity	0.02	0.05
polyethylene	1.9×10^{-7}	8.3×10^{-8}
activated carbon blended		
0.135%	2.9×10^{-7}	1.4×10^{-7}
1%	9.6×10^{-7}	5.0×10^{-7}
5%	4.0×10^{-6}	2.2×10^{-6}
Tenax blended		
3.9%	4.9×10^{-7}	2.6×10^{-7}

Table 14. Maximum calculated sorption capacity for toluene

vapor activity	0.02	0.05
polyethylene	1.7×10^{-6}	7.2×10^{-6}
activated carbon blended		
0.135%	2.1×10^{-6}	7.4×10^{-6}
1%	5.0×10^{-6}	8.7×10^{-6}
5%	1.8×10^{-5}	1.5×10^{-5}
Tenax blended		
3.9%	2.8×10^{-6}	7.9×10^{-6}

The values of C_s versus concentration of blended activated carbon in film samples (wt%) and S_{max} are plotted in Figures 21, 22 and 23. Figures 24 and 25 show relationship between the sorption coefficient of limonene in polyethylene samples having different surface area per unit mass, and the values of the area per unit of mass for each sample, respectively.

In Figure 21, it appears to reach the equilibrium at 5 wt% of concentration of activated carbon at lower vapor activity. On the other hand, there is very little difference of sorption coefficient among 3 blended concentrations at higher vapor activity. This result suggests that limonene may saturate the 0.135 wt% of activated carbon. This shows that activated carbon is effective at low concentration of limonene by a factor of almost 2. To compare experimental data and S_{max} data of 0.135 wt% blended concentration, experimental data shows higher values than S_{max}. Most of other data are below the estimated S_{max} values. These results would suggest all activated carbon did not sorb limonene.

When the sorbate is ethyl acetate, the graphs for both the lower and higher vapor activity levels showed the equilibrium at 5 wt% of blended activated carbon, as shown in Figure 22. It means both lower and higher concentration of sorbate would be sorbed by 5 wt% of blended activated carbon. To compare experimental data and S_{max}, almost same tendency as limonene is observed. These results would suggest all activated carbon did not sorb ethyl acetate.

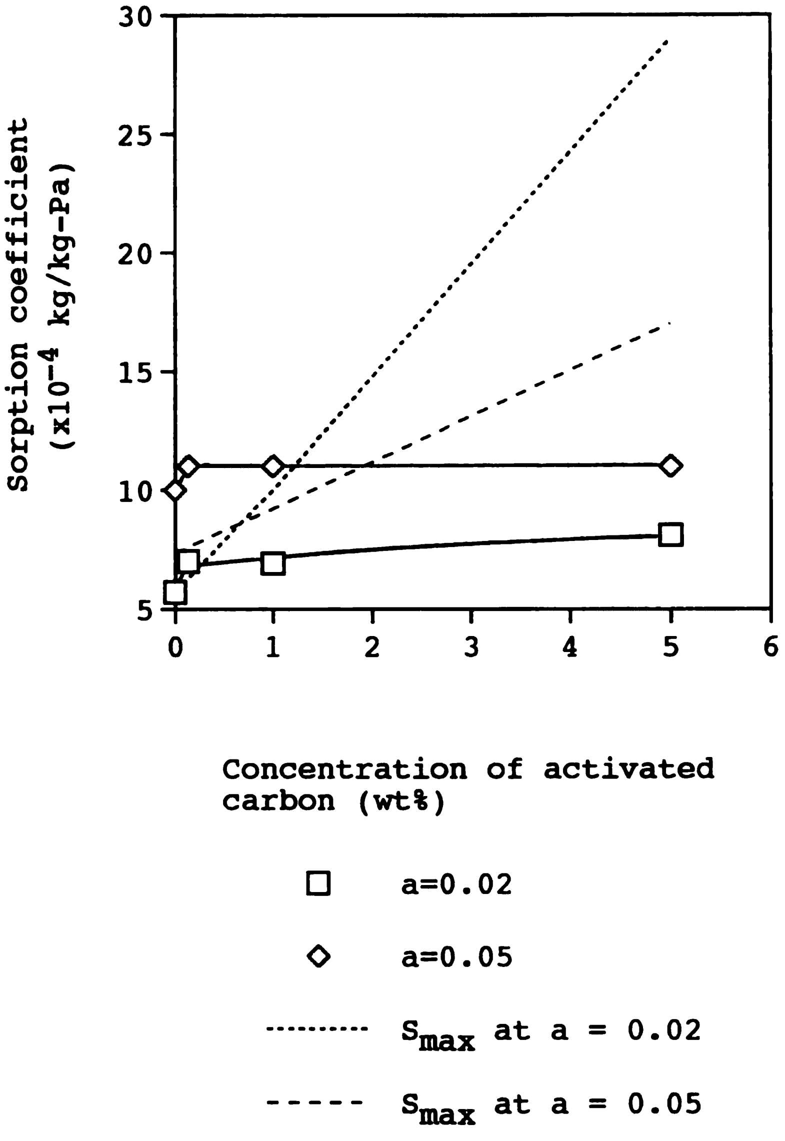


Figure 21. Relationship between concentration of activated carbon blended in a film and sorption coefficient of limonene

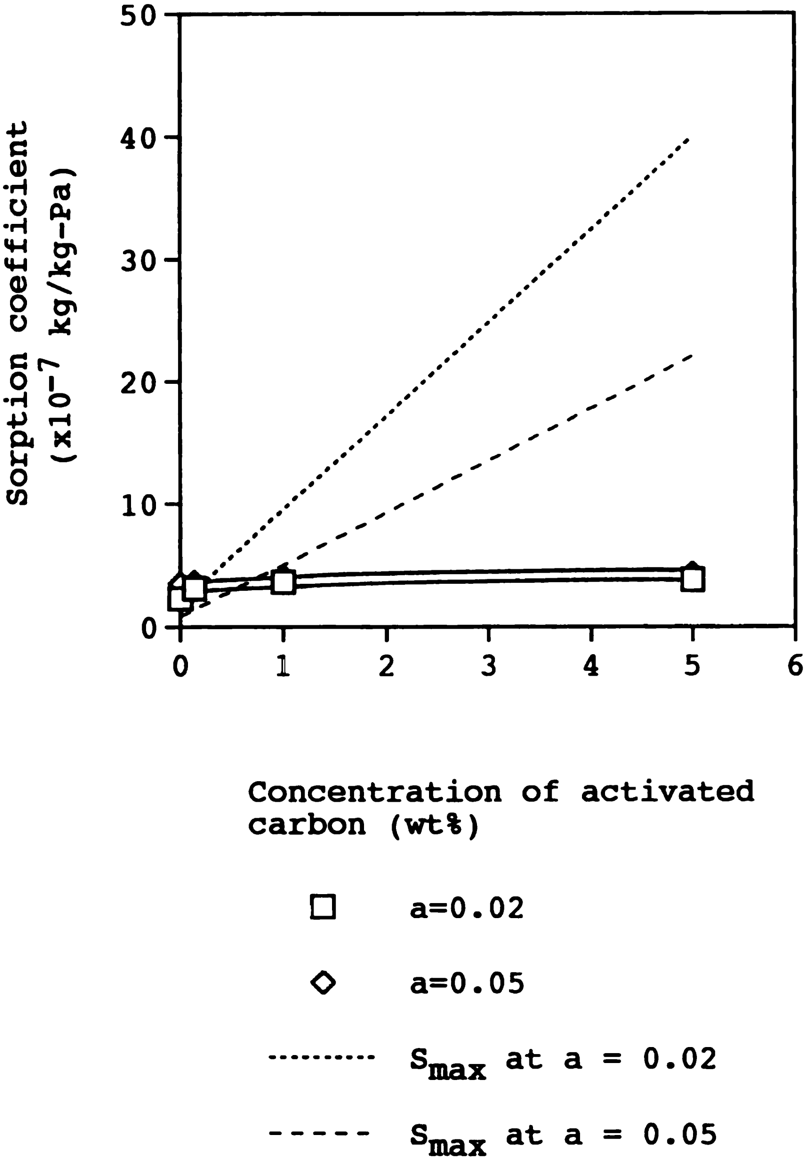


Figure 22. Relationship between concentration of activated carbon blended in a film and sorption coefficient of ethyl acetate

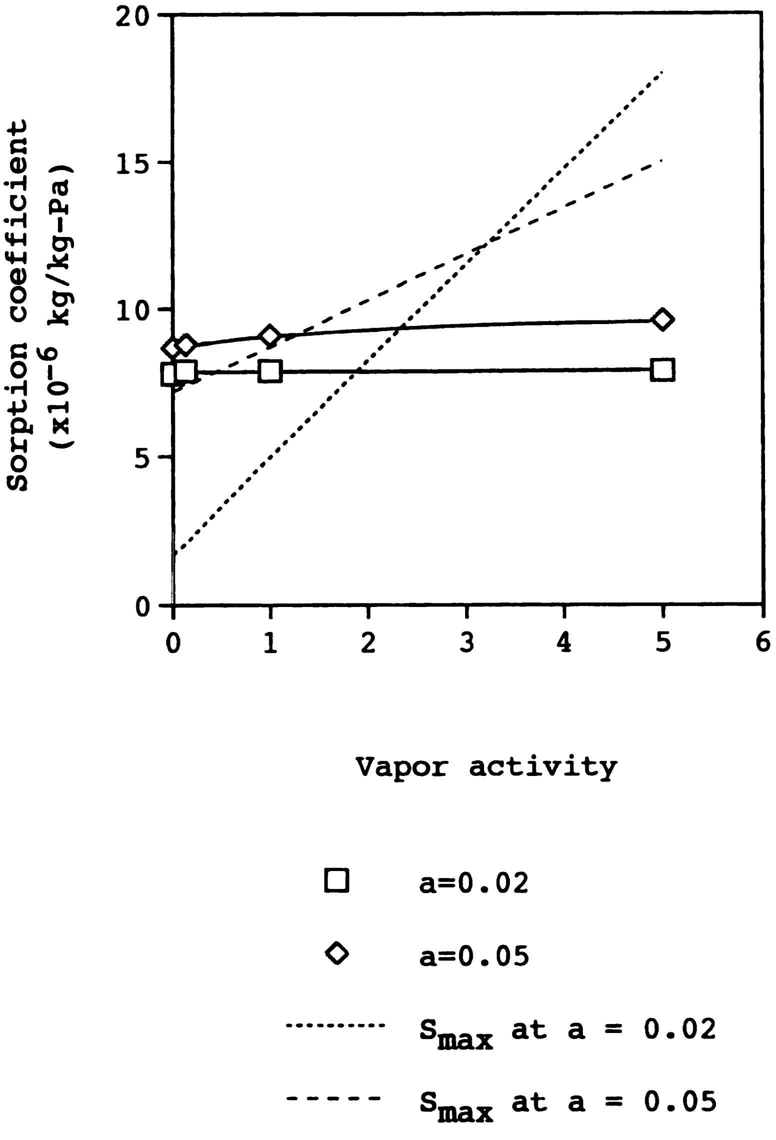


Figure 23. Relationship between concentration of activated carbon blended in a film and sorption coefficient of toluene

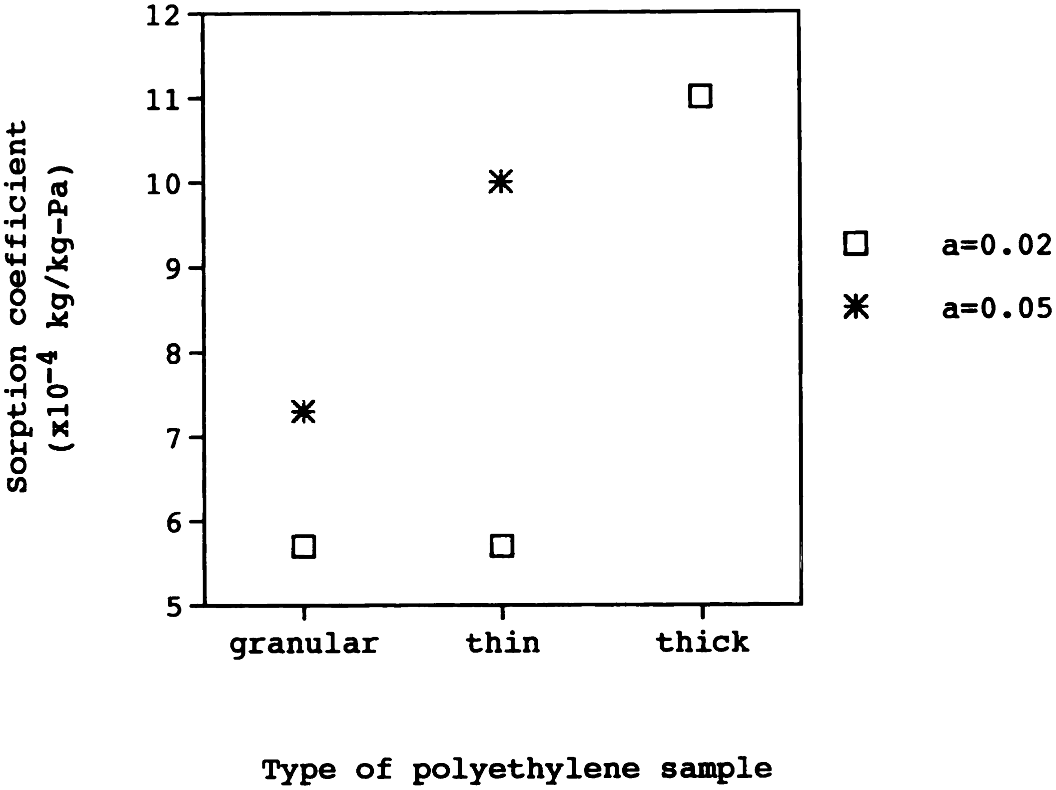
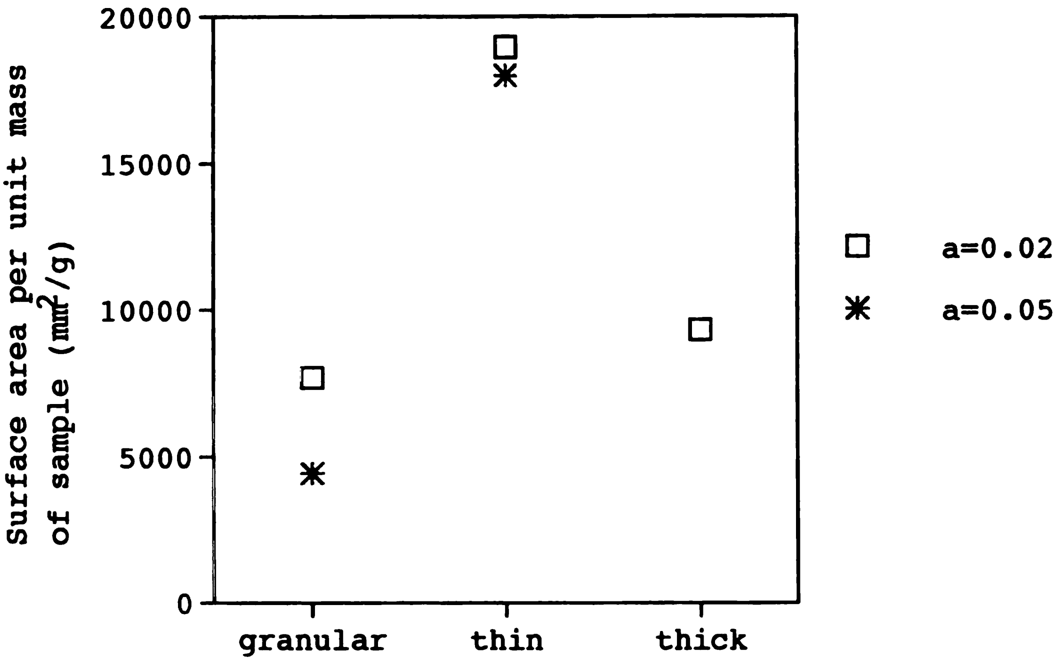


Figure 24. Relationship between sorption coefficient of limonene and type of polyethylene sample



Type of polyethylene sample

Figure 25. Relationship between surface area per unit mass and type of polyethylene sample

For toluene, Figure 23 shows very little sorption coefficient difference among 3 concentrations of blended activated carbon. It means 0.135 wt% of activated carbon can sorb such low concentration of toluene. As contrasted with this result, the higher concentration of toluene (a=0.05) may need more than 5 wt% of activated carbon to sorb. To compare experimental data and S_{max} data, almost same tendency as other sorbates is observed: for 0.135 wt% blended concentration, experimental data shows higher values than S_{max}. Most of other data are below the estimated S_{max} values. These results would suggest all activated carbon did not sorb toluene.

It seems that all these results show the curvilinear sorption behavior in these blended concentration of this sorbate. The sorption of polyethylene would also happen on these samples, however, activated carbon may sorb more amounts of sorbate than polyethylene. But such an analysis is inconclusive given the small data set.

Tenax blended film sorbed very little limonene. However, it sorbed more ethyl acetate and toluene than the activated carbon blended film. On the other hand, activated carbon blended film sorbed greater sorbate amounts overall than polyethylene film. So, it can be said activated carbon has more capacity but no selective sorption characteristics for these three organic substances.

Tenax alone sorbed two times or more limonene than pure polyethylene. This may suggest some hindrance phenomena or the inacceptibity of Tenax in polyethylene to reach limonene.

From the optical observations, some particles of Tenax are completely surrounded by polyethylene, that may support the latter presumption. As shown in Table 1, Tenax has relatively large pores on its surface. Therefore, polyethylene would be packed more easily than activated carbon, and interrupt sorption of large molecules such as limonene.

From Equation 1, the number of volatile molecules striking the surface every second, n, was calculated for each organic compound and vapor activity at test temperature. They are shown in Table 12.

Table 15 shows limonene is able to be sorbed about half the number of molecules as the other two sorbates. This is due to its large molecular weight.

Table 15. The number of molecules of organic compound striking the surface of sorbents per second (molecules/cm^2/sec)

vapor activity	0.02	0.05
limonene	$4.74x10^{17}$	$1.19x10^{18}$
ethyl acetate	$9.11x10^{17}$	$2.28x10^{18}$
toluene	$8.52x10^{17}$	$2.13x10^{18}$

The uptake by the sorbent is so low or below expected for both two sorbents. Two reasons may be considered to explain this question. First, the sorption process needs very long time to reach equilibrium. Therefore, the blended sample films haven't reached the equilibrium. Secondly, there may be some problem at the interface between sorbents and polyethylene. If there is any interaction between them, it may interrupt the sorption behavior. These have not satisfactory answered yet.

From the results of comparison of sorption coefficient of several different polyethylene samples (Table 11, and Figures 24 and 25), two thin polyethylene films show completely different sorption coefficients even though their values of surface area per unit mass are very close. This appears to be dependent upon the concentration of sorbate, but such an analysis is inconclusive given the small data set.

Possible sources of experimental errors are listed as follows:

1. Sensitivity of electrobalance.

Since the electrobalance is very sensitive, it must be placed where external vibrations are minimized. External vibrations may cause fluctuation of the equipment sensitivity.

2. Gas flow regulator.

Due to the sensitivity of the electrobalance and the tubing system, vapor concentration cannot be easily checked during the course of the experiment. Sometimes the gas flow regulator affected the results with noise generation. In addition, a small change of vapor concentration can result in a large measured weight increase for the sample film. Consequently, the flow regulators used must be accurate and precise to generate an identical flow rate during the test and between subsequent runs. Also, the nitrogen gas used to generate proper vapor concentration had to be checked to maintain constant pressure throughout the experiment. No action was taken during this study to minimize these effects.

3. Distribution of sorbents.

When sample films were made by a laboratory press, both activated carbon and Tenax tended to spread to the edge of the film with the flow of melted polyethylene. Therefore, there were some parts of the sample film which had different sorbent concentrations. For this sorption study, the test films were visually checked to ensure sorbent concentrations were as equal as possible.

4. Temperature of testing environment.

Sorption is temperature dependent. Even though the laboratory is air conditioned, room temperature changes easily due to weather, number of people in the room, and so on. Hence, the electrobalance system should be in a well-controlled, temperature-stabilized chamber.

5. Static electricity in the hangdown tube.

If static charge develops inside the hangdown tube, it attracts the wire of the electrobalance. If the wire touches the wall of hangdown tube, the detected weight will differ greatly from actual weight. Therefore, it is important to minimize static electric buildup in the electrobalance system.

Summary

(1) Tenax showed a larger decrease in density than activated carbon when both were blended with polyethylene. Even the weight of blended Tenax film samples is lower than that of blended activated carbon. This is caused by the density difference of these sorbents.

(2) It was observed that the greater the concentration of blended sorbents, the poorer the mechanical properties of both materials. However, a linear relationship between concentration of Tenax and elastic modulus is observed. On the other hand, a logarithmic relationship is shown for activated carbon. This phenomena may be caused by the difference of size of sorbent particles. The particle size of activated carbon is much smaller than that of Tenax. Therefore, Tenax blended polyethylene could lose its flexibility easier than activated carbon blended samples.

(3) It is observed by optical observation that some particles of sorbent are completely surrounded by polyethylene. There is less destruction of physical structure of Tenax than expected, even though the thickness of the sample film is almost half of the average diameter of Tenax.

(4) Tenax blended film sorbed very little limonene. However, it showed more sorption than activated carbon blended film for ethyl acetate (1.2 times) and toluene (1.1 times). On the other hand, activated carbon blended film sorbed greater amounts of all other sorbates than polyethylene (limonene: 1.1~1.4 times; ethyl acetate: 1.0~1.7 times; toluene: 1.0~1.1 times). Tenax can sorb limonene when it is granular. This selective sorption characteristic may be caused by polyethylene which can be packed into the porous structure of Tenax. This is not confirmed on this study.

(5) From the result of comparison of sorption coefficients of several types of polyethylene samples, two thin polyethylene films show completely different sorption characteristics, even though their values of surface area per unit mass are very close. This appears to be concentration dependent, but that is difficult to conclude from these data. A more extensive database would be required to resolve that issue.

(6) The uptake by the sorbent is so low or below expected for both two sorbents. Two reasons may be considered to explain this question. First, the sorption process needs very long time to reach equilibrium. Therefore, the blended sample films haven't reached the equilibrium. Secondly, there may be some problem at the interface between sorbents and polyethylene. If there is

any interaction between them, it may interrupt the sorption behavior. These have not satisfactory answered yet.

Future Studies

(1) To confirm the sorption characteristics of sorbent blended samples, electron microscopic observation of the specific case of sorbent which is completely enveloped in polyethylene would be helpful. This method would provide a visual representation of the surface of the sorbent, so the effect of polyethylene on the sorbent's porous structure would be clarified.

(2) To give better sorption characteristics, the blending of multiple sorbents into polyethylene could be considered. Multiple sorbents may provide more uniform sorbent coverage of organic volatiles, by closing the gaps in coverage left by individual sorbents.

Appendix A

Blending Sorbents into Polyethylene

Appendix A

Blending Sorbents into Polyethylene

Materials:

Low density polyethylene
(LDPE, Dow Chemical U.S.A., Freeport, TX)
Tenax-TA®
(80/100 mesh, Alltech Associates, Inc., Deerfield, IL)
Activated carbon
(Norit® A, 100 mesh, Fisher Scientific, Fair Lawn, NJ)
Baker-Perkins MP2030 Compounder
(Baker-Perkins, Saginaw, MI)
Extruder model KLB-100
(Killion Extruders Inc., Cedar Grove, NJ)

Concentrations of 1.6, 2.8 and 3.9 % (w/w) Tenax, 0.135, 1 and 5 % (w/w) activated carbon in LDPE, respectively, were made for the sorption tests.

1. Determination of Sampling Time

The determination of the residence time distribution in an extruder was important to control the concentration of blended sorbents because the concentration of sorbents in LDPE increased gradually after putting them into an extruder. Therefore, to determine the sampling time of blended LDPE the residence time distribution was measured.

Butler (1990) reported a study of the residence time distribution for processing because most polymers are heat sensitive. Butler's procedure was applied for the determination of sampling time.

1. Turn on the extruder (Baker-Perkins, Saginaw, MI) to preheat. The temperature and processing conditions of the extruder were:

Temperatures:

section 1: 150 °C

section 2: 150 °C

section 3: 150 °C

die: 150 °C

Screw speed: 70 rpm

Automatic LDPE feed rate: 4 %

2. The extruder was purged about 30 minutes using LDPE which was same grade as test samples.

3. Set the screw speed and confirm the rate of extrusion. To confirm the rate of extrusion, the weight of extruded LDPE per minute was measured.

4. After enough purging and stabilized extruding, 0.02 grams of activated carbon were added from the hopper every two minutes for a total of eight times during the extrusion of LDPE. This activated carbon worked as a pigment and was used as a controlling variable.

5. The extruded LDPE were sampled every one minute, and their colors were determined by comparing to a color gradient chart. The color gradient chart is shown as Figure 43.

6. The color gradient vs. extruding time was plotted to determine time when the stable concentration of sample was obtained. This plot is shown as Figure 44. In Figure 44, the times carbon were added are represented as symbol ∇.

From Figure 44, a sampling time from the extruder of 17 to 26 minutes was selected after the sorbent was admitted.

2. Blending Tenax and LDPE

Tenax blended LDPE pellets were made using a Baker-Perkins MP2030 Compounder. The procedure was as follows:

1. Turn on the extruder to preheat. The temperature and processing conditions of the extruder were:

Temperatures:

section 1: 150 °C

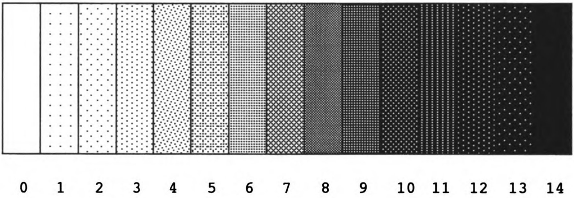


Figure 26. Color gradient chart

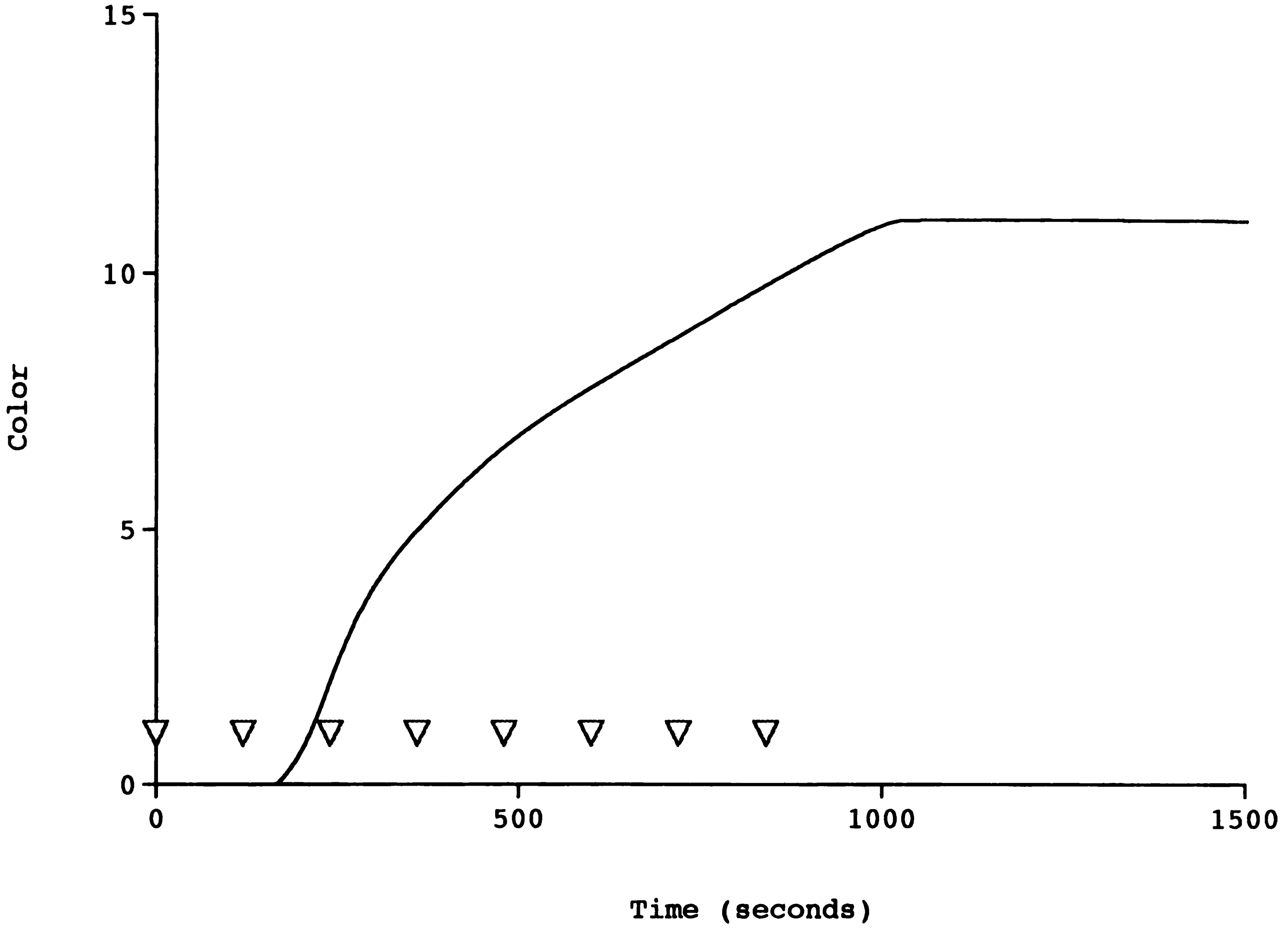


Figure 27. Relationship between extruding time and color gradient

section 2: 150 °C
section 3: 150 °C
die: 150 °C
Screw speed: 70 rpm
Automatic LDPE feed rate: 4 %

2. The extruder was purged about 30 minutes using LDPE which was of the same grade as the test samples.

3. Set the screw speed and confirm the rate of extrusion. To confirm the rate of extrusion, the weight of extruded LDPE per minute was measured.

4. After sufficient purging and stabilized extruding, certain amounts of Tenax were added from the hopper while extruding LDPE. The amount of Tenax was determined by the rate of extrusion.

For example, when the rate of extrusion was 6 grams per minute, Tenax was added 0.3 grams per minutes for 5 % (w/w).

5. Using a pair of nippers, the blended polymer was pelletized. The pelletized blended resins were stored far from any organic substances to avoid contamination.

3. Making Activated Carbon Blended LDPE

Activated carbon blended LDPE pellets were made using an extruder (model KLB-100, Killion Extruders, Inc., Cedar Grove, NJ). The procedure was as follows:

1. Turn on the extruder to preheat. The temperature and processing conditions of the extruder were:

    Temperatures:

        section 1: 270 °F (132 °C)
        section 2: 350 °F (177 °C)
        section 3: 365 °F (185 °C)
        die: 320 °F (160 °C)

    Screw speed: 10 rpm

2. The extruder was purged about 30 minutes using LDPE which was the same grade as the test samples.

3. Set the screw speed and confirm the rate of extrusion. To confirm the rate of extrusion, the weight of extruded LDPE per minute was measured.

4. After sufficient purging and stabilization of extrusion, LDPE resins mixed with certain amounts of activated carbon were added from the hopper. The amounts of activated carbon were determined by weight basis.

    For example, 0.5 grams of activated carbon were mixed to 9.5 grams of LDPE to make 5 % (w/w) concentration.

5. Using a pair of nippers, the blended polymer was pelletized. The pelletized blended resins were stored far from any organic substances to avoid contamination.

Appendix B

Procedure for Making Film Samples

Appendix B

Procedure for Making Film Samples

Materials:

Low density polyethylene (LDPE, DuPont Chemical Co.)

Tenax-TA® blended LDPE pellets

Activated carbon blended LDPE pellets

Carver Laboratory Press (Model M, Fred S. Carver Inc.)

PET sheets

Procedure:

All concentrations of Tenax and carbon blended LDPE pellets were processed to film for sorption tests.

1. The laboratory press was preheated prior to resin set up. The temperature condition for both platens was 150 °C.

2. When 150 °C was reached, the sample resins were set on the bottom platen and covered with two sheets of PET as shown as Figure 45.

3. 30000 psi of pressure was applied 10 minutes to make a

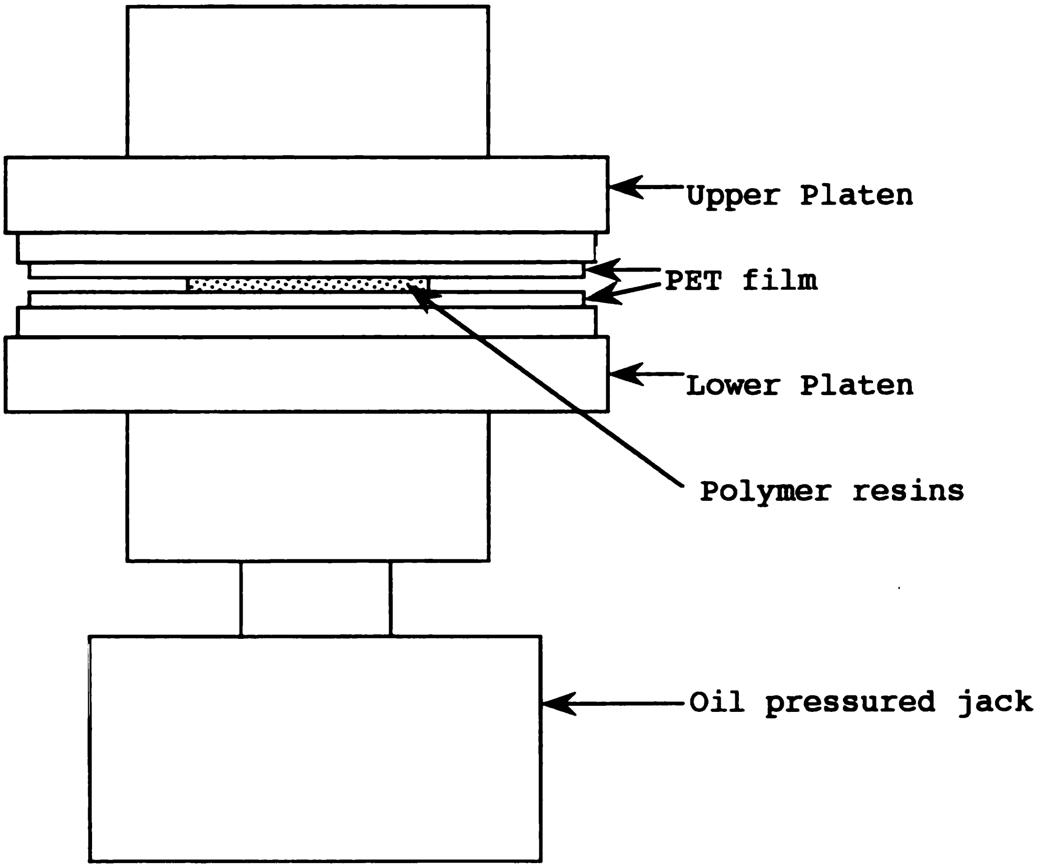


Figure 28. Schematic of laboratory press

thin layer of blended polymers.

4. After 10 minutes of applied pressure, these platens were cooled to 70 °C by water. During this cooling period, 30000 psi of pressure was applied.

5. When the temperature reached 70 °C, the pressure was released from the platens and the sample film was collected. All sample films were stored far from any organic substances to avoid contamination.

Appendix C

Procedure for the Determination of Absorbate Calibration Curve by Gas Chromatography

Appendix C

Procedure for the Determination of Sorbate Calibration Curve by Gas Chromatography

Materials:

Four 25 ml volumetric flasks with stoppers and two 50 ml volumetric flasks with stoppers were used to prepare standard solutions.

A 10 μl liquid sampling syringe was used to inject samples into the gas chromatograph.

A 10 ml pipette and four 1 ml pipettes were used to adjust the concentrations in the preparation of standard solutions.

A Hewlett Packard HP5890A gas chromatograph with flame ionization detector (FID) was used to quantify the sorbates in the standard solutions (Hewlett-Packard, Avondale, PA).

(R)-(+)-limonene (97%) was obtained from Aldrich Chemical Company (Milwaukee, WI). Toluene (99.9%) was obtained from Mallinckrodt Inc. (Paris, KY), and ethyl acetate (100%) was secured from J. T. Baker Chemical Company (Phillipsburg, NJ). They were used as sorbates in this study.

Dichloromethane (DCM, 99.5%) and o-dichlorobenzene (DCB, 98%) were obtained from EM Science (Gibbstown, NJ). DCM was used as a solvent for limonene and toluene, and DCB was used as a solvent for ethyl acetate.

Concentrations of 5, 10, 20, 50, and 100 ppm (v/v) of sorbate in solvent were prepared to make the calibration curves.

Procedure:

The standard curves of the injected sorbate quantities vs. responded area units for all the sorbates were constructed using standard solutions of known concentrations. The standard solutions were prepared by dissolution of known quantities of both limonene and toluene in dichloromethane and ethyl acetate in dichlorobenzene. To prepare the calibration curves, the following steps were applied:

1. The flasks and the syringe were heated overnight in an oven at 80 °C to remove or reduce any residual organic compounds that could be adsorbed on the flasks' walls prior to use. The flasks were then left covered at room temperature prior to utilization.

2. The purity of the solvents, DCM and DCB, were tested on the gas chromatograph to verify the existence of interfering peaks near the solvents' retention times. 1 μl of pure solvent was injected into each of the solvents, and no interfering peak was observed on either solvent.

3. The standard solutions were prepared by the following dilution steps:

   a) One 50 ml volumetric flask was partially filled with solvent using a 10 ml pipette.
   b) 0.5 ml of sorbate was added into the 50 ml flask.
   c) A stopper was set and the flask was slightly swirled to mix.
   d) The flask was filled to volumetric line with the solvent.
   e) A stopper was set and the flask's contents were mixed completely.

The procedure shown above provided the 10000 ppm stock solution. From this stock solution, the other concentrations of standard solutions were obtained by following dilution steps:

   a) One 50 ml volumetric flask was partially filled with solvent using a 10 ml pipette.
   b) The flask of stock solution was swirled to ensure proper mixing.
   c) 0.5 ml of stock solution was added into the partially filled flask.
   d) A stopper was set and the flask was slightly swirled to mix.
   e) The flask was filled to volumetric line with the solvent.
   f) A stopper was set and the flask's contents were mixed

completely.

The procedure shown above provided the 100 ppm standard solution. The other concentrations were obtained by similar procedures.

4. The analyzing conditions of the gas chromatograph were set as shown below.

Column:

SUPELCOWAX™ 10
Fused Silica Capillary Column
60 m, 0.25 mm I.D., 0.25 μm film thickness

Analysis Conditions:

Initial temperature	75 °C
Initial time	8.0 min.
Rate	4.0 °C/min.
Final temperature	200 °C
Final time	4.0 min.
Injection temperature	200 °C
Detector temperature	250 °C
Helium gas flow	30 ml/min.

5. A 1 μl sample was injected directly into the gas chromatograph and the corresponding area units were recorded for each concentration of sorbates.

6. The corresponding area units (A.U.) of the gas chromatograph versus the quantities of injected sorbates were plotted and a linear relationship was observed for each sorbate. The slope of this curve equals the calibration factor. The data and standard curves were shown in Table 11 ~ 13 and Figure 40 ~ 42 for all sorbates, respectively. In addition, the calibration factors (C.F.) were determined from the slope of calibration curves.

C.F. for limonene = 3.47×10^{-12} g/A.U.

C.F. for ethyl acetate = 1.19×10^{-11} g/A.U.

C.F. for toluene = 2.53×10^{-12} g/A.U.

Table 16. Data for calibration curve of limonene

Concentration (ppm)	Volume injected(g)	Area Unit*
5	$4.20x10^{-9}$	942
10	$8.40x10^{-9}$	2399
20	$1.68x10^{-8}$	3895
50	$4.20x10^{-8}$	13644
100	$8.40x10^{-8}$	23299

* retention time = 11.6 min.

Table 17. Data for calibration curve of ethyl acetate

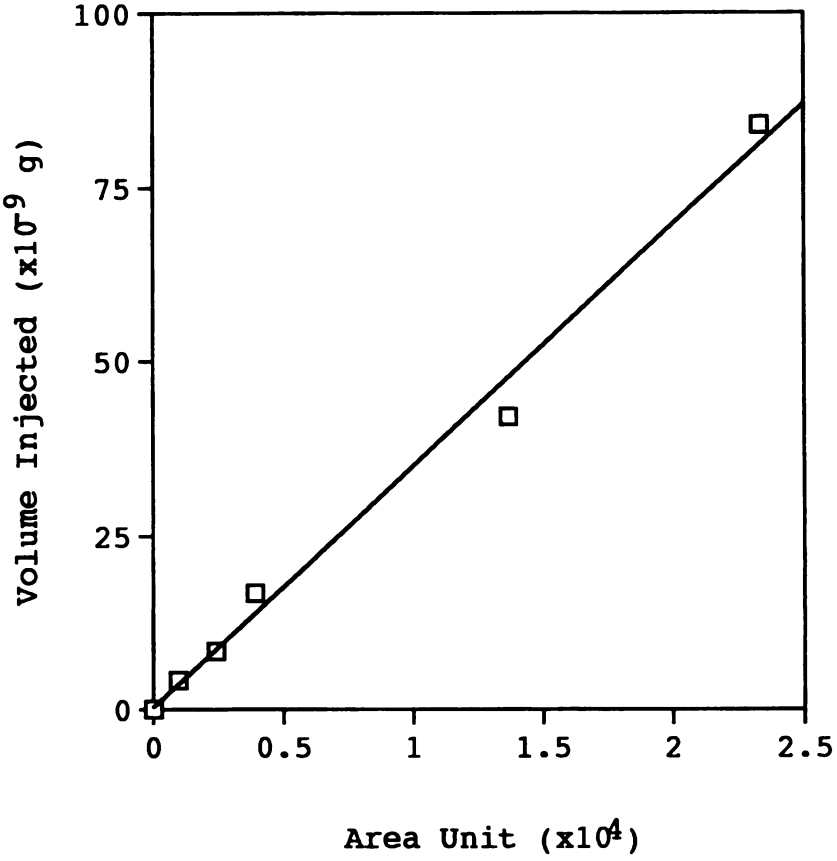
Concentration (ppm)	Volume injected(g)	Area Unit*
5	$4.47x10^{-9}$	354
10	$8.93x10^{-9}$	751
20	$1.79x10^{-8}$	1485
50	$4.47x10^{-8}$	3728
100	$8.93x10^{-8}$	7472

* retention time = 4.8 min.

Table 18. Data for calibration curve of toluene

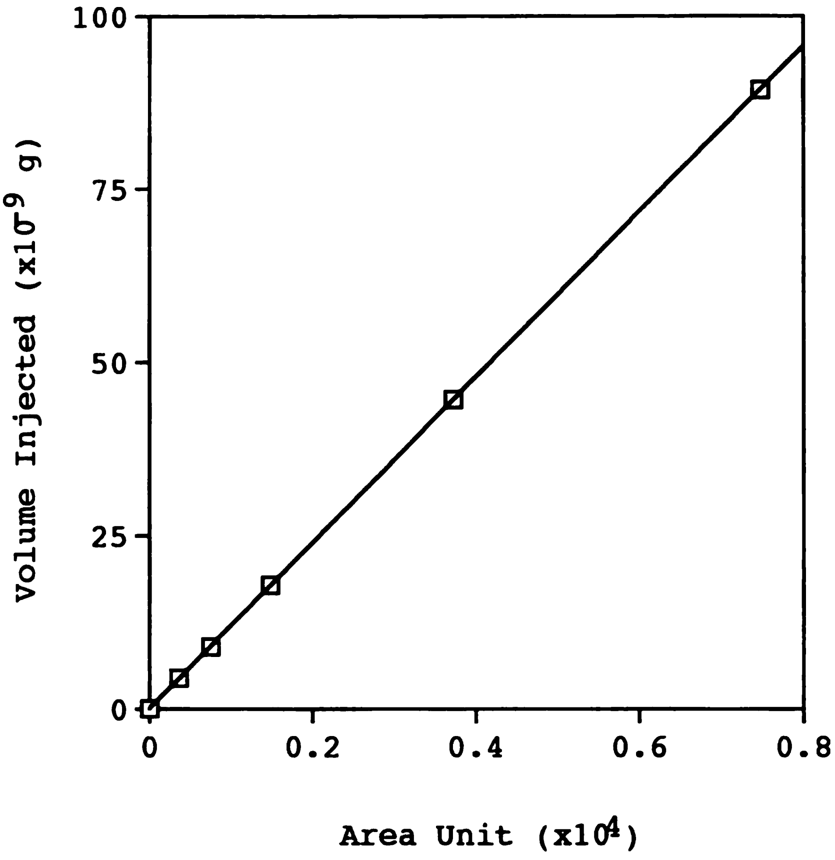
Concentration (ppm)	Volume injected(g)	Area Unit*
5	4.34×10^{-9}	2285
10	8.67×10^{-9}	3811
20	1.73×10^{-8}	8142
50	4.34×10^{-8}	19456
100	8.67×10^{-8}	34033

* retention time = 6.8 min.



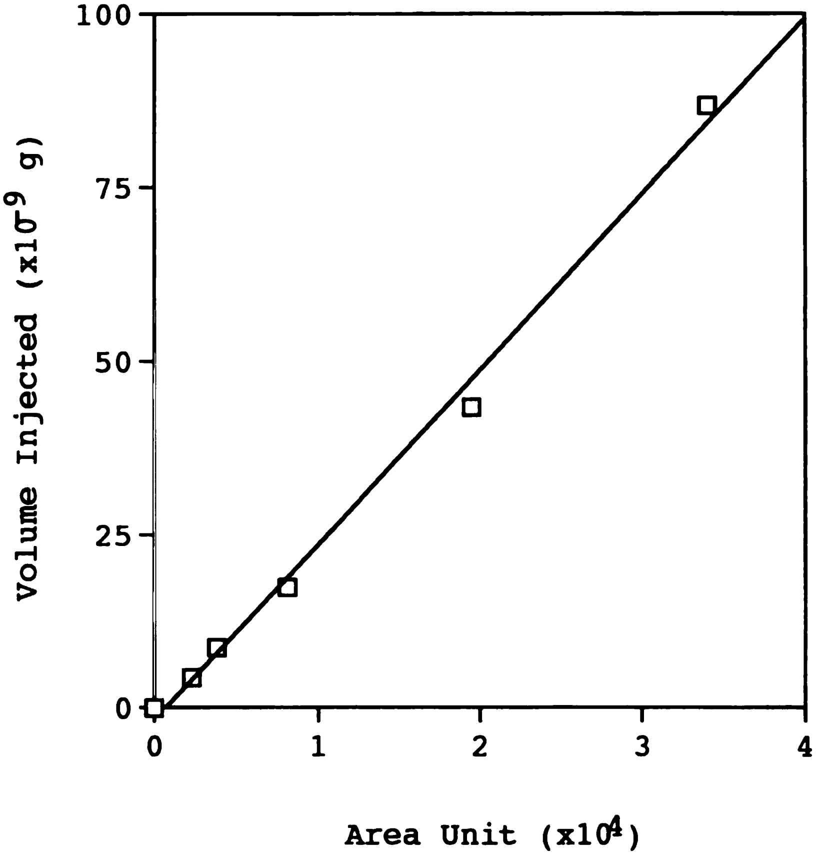
Volume Injected = $3.47 \times 10^{-12} \times$A.U.$+3.68 \times 10^{-10}$
$r^2 = 0.990$

Figure 29. Calibration Curve for Limonene



Volume Injected = $1.19 x 10^{-11}$xA.U.+$8.52x10^{-11}$
$r^2 = 1.000$

Figure 30. Calibration Curve for Ethyl Acetate



Volume Injected = $2.53\times10^{-12}\times A.U.-1.77\times10^{-9}$
$r^2 = 0.995$

Figure 31. Calibration Curve for Toluene

Bibliography

Bibliography

Baner, A.L., R.J.Hernandez, K.Jayaraman, and J.R.Giacin. 1986. Current technology in flexible packaging. ASTM STP 912:49

Bentley, D.J.Jr., 1988. A guide to FDA regulation of adhesives and coatings for flexible packaging. Tappi Journal, September, p 125

Bigg, D.M. 1992. The newest developments in polymeric packaging materials. IoPP Technical Journal, Fall, p 24

Billmeyer, F.W.Jr. 1984. Textbook of Polymer Science. John Wiley & Sons, Inc., New York

Butler, T.I. 1990. The influence of extruder residence time distribution on polymer degradation. Journal of Plastic film & Sheeting, 6:247

Cheremisinoff, P.N., and A.C.Morresi. 1978. Carbon adsorption applications. Ch. 1. In Carbon adsorption handbook, P.N. Cheremisinoff, F. Ellerbusch (Eds.), p 1. Ann Arbor Science, Ann Arbor, MI.

Cookson, J.T.Jr. 1978. Adsorption mechanisms: The chemistry of organic adsorption on activated carbon. Ch. 7. In Carbon adsorption handbook, P.N. Cheremisinoff, F. Ellerbusch (Eds.), p 241. Ann Arbor Science, Ann Arbor, MI.

Daemen, J.M., W.Dankelman, and M.E.Hendriks. 1975. Properties and applications of Tenax GC as a column packing material in gas chromatography. Journal of Chromatographic Science, 13:79

Darco, Atlas Chemical Div., ICI America, Inc., 1965. Darco powdered and granular activated carbon. Wilmington, DE.

DeLassus, P.T., J.C.Tou, M.A.Babinec, D.C.Rulf, B.K.Karp, and B.A.Howell. 1988. Transport of apple aromas in polymer films. Ch. 2. In Food and Packaging Interactions, J.H. Hotchkiss (Ed.), p 11. ACS Symposium Series 365. American Chemical Society, Washington, DC.

Dixon, J.B., and S.B.Weed. 1977. Minerals in Soil Environments, Soil Sci. Soc. Amer., Inc. Madison, WI.

Flory, P.J. 1953. Principles of Polymer Chemistry. Cornell University Press, Ithaca, NY.

Food and Drug Administration, Department of Health and Human Services. 1993. Title 21 of the Code of Federal Regulations, Part 177, section 1010-2000. U.S.Government Printing Office, Washington, DC.

Foster, R.H. 1987. Ethylene vinyl alcohol copolymer resins for better solvent, aroma and flavor barrier. Future-Pac, 5th International Conference on Packaging Innovations, Atlanta GA, Ryder Associates.

Frissel, M.J. 1961. The Adsorption of Some Organic Compounds, Especially Herbicides, on Clay Minerals, Wageningen, Centrum voor Landbouwpublikaties en Landbouwdocumentatie.

Heaver, D.L., M.W.Ogden, and P.R.Neison. 1992. Multisorbent thermal desorption/gas chromatography/mass selective detection method for the determination of target volatile organic compounds in indoor air. Environ. Sci. Technol., 26(9):1737

Heckman, J.H. 1991. Packaging industries and the food-additives amendment. Ch. 8. In Food and Packaging Interactions II, J.H. Hotchkiss (Ed.), p 88. ACS Symposium Series 473. American Chemical Society, Washington, DC.

Hernandez, R.J., J.R.Giacin, and A.L.Baner. 1986. Measuring the aroma barrier properties of polymeric packaging materials. Pkg. Technol., 16(4):12

Hirose, K., B.R.Harte, J.R.Giacin, and J.Miltz. 1988. Sorption of d-limonene by sealant films and effect on mechanical properties. Ch. 3. In Food and Packaging Interactions, J.H. Hotchkiss (Ed.), p 28. ACS Symposium Series 365. American Chemical Society, Washington, DC.

Hotchkiss, J.H. 1988. An overview of food and food packaging interactions. Ch. 1. In Food and Packaging Interactions, J.H. Hotchkiss (Ed.), p 28. ACS Symposium Series 365. American Chemical Society, Washington, DC.

Huggins, M.L. 1942. Thermodynamic properties of solutuion of long-chain compounds. Annals of the New York Academy of Science, 43:1

Imai, T. 1988. Absorption of organic volatiles by sealant films. M.S. thesis, Michigan St. Univ., East Lansing

Konczal, J.B., B.R.Harte, P.Hoojjat, and J.R.Giacin. 1992. Apple juice flavor compound sorption by sealant films. Journal of Food Science, 57(4):967

Kovach, J.L. 1978. Gas-phase adsorption and air purification. Ch. 9. In Carbon adsorption handbook, P.N. Cheremisinoff, F. Ellerbusch (Eds.), p 331. Ann Arbor Science, Ann Arbor, MI.

Kwapong, O.Y., and J.H.Hotchkiss. 1987. Comparative sorption of aroma compounds by polyethylene and ionomer food-contact plastics. Journal of Food Science, 52(3):761

Labuza, T.P., and W.M.Breene. 1989. Applications of "Active packaging" for improvement of shelf-life and nutritional quality of fresh and extended shelf-life foods. Journal of Food Processing & Preservation, 13:1

Marshall, M.R., J.P.Adams, and J.W.Williams. 1985. Flavor absorption by aseptic packaging materials. Proceedings ASEPTIPAK '85. Third International Conference and Exhibition on Aseptic Packaging, Princeton, NJ.

Modern Plastics Encyclopedia '91. 1990. Mid-October 1990 issue, 67:11

Mohney, S.M., R.J.Hernandez, J.R.Giacin, B.R.Harte, and J.Miltz. 1988. Permeability and solubility of d-limonene vapor in cereal package liners. Journal of Food Science, 53(1):253

Mortland, M.M. 1970. Clay-organic complexes and interactions. Adv. Agron., 22:75

Mortland, M.M. 1986. Mechanisms of adsorption of nonhumic organic species by clays. Interaction of Soil Minerals with Natural Organics and Microbes. Soil Sci. Soc. Amer., Madison, WI.

Parliament, T.H. 1987. Sample analysis in flavor and fragrance research. American Lab., 19(1):51

Patton, G.W., L.L.McConnell, M.T.Zaranski, and T.F.Bidleman. 1992. Laboratory evaluation of polyurethane foam-granular adsorbant sandwich cartridges for collecting chlorophenols form air. Anal. Chem. 64:2858

Perry, R.H., D.W.Green, and J.O.Maloney. 1984. Perry's Chemical engineers' handbook, McGraw-Hill chemical engineering series, McGraw-Hill, Inc., New York

Roland, A.M., and J.H.Hotchkiss. 1991. Determination of flavor-polymer interactions by vacuum-microgravimetric method. Ch. 13. In Food and Packaging Interactions II, J.H. Hotchkiss (Ed.), p 149. ACS Symposium Series 473. American Chemical Society, Washington, DC.

Sacharow, S. 1991. Packaging meets 1990s needs through active technology. Paper, Film & Foil Converter, July, p 52

Sakodynskii, K., L.Panina, and N.Klinskaya. 1974. A study of some properties of Tenax, a porous polymer sorbent. Chromatographia, 7(7):339

Schroeder, M.A. 1989. Effect of sorption of flavor volatiles on the adhesive and cohesive bond strength of multilayer laminations. M.S. thesis, Michigan St. Univ., East Lansing

Sharp, G.J., Y.Yokouchi, and H.Akimoto. 1992. Trace analysis of organobromine compounds in air by adsorbent trapping and capillary gas chromatography/mass spectroscopy. Environ. Sci. Technol. 26:815

Strandburg, G., P.T.DeLassus, and B.A.Howell. 1991. Thermodynamics of permeation of flavors in polymers. Ch. 12. In Food and Packaging Interactions II, J.H. Hotchkiss (Ed.), p 133. ACS Symposium Series 473. American Chemical Society, Washington, DC.

Van Wijk, R. 1970. The use of poly-para-2,6-diphenyl-phenylene oxide as a porous polymer in gas chromatography. Journal of Chromatographic Science, 8:418

Vejrosta, J., M.Mikesova, A.Ansorgova, and J.Drozd. 1988. Sorption of benzene on Tenax. Journal of Chromatography, 447:170

Vejrosta, J., M.Mikesova, and J.Drozd. 1989. Sorption of n-alkanes on Tenax. Journal of Chromatography, 464:394

Wagner, B., and N.Vaylen. 1990. The packaging activists. Prepared Foods, 159:172

Weber, W.J.Jr., 1972. Physicochemical processes for water quality control. John Wiley & Sons, New York