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IMPACT OF POLYMER PROCESSING ON SORPTION OF BENZALDEHYDE VAPOR IN RUBBERY POLYPROPYLENE

By

Ying Qin

A THESIS

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

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ABSTRACT

IMPACT OF POLYMER PROCESSING ON SORPTION OF BENZALDEHYDE VAPOR IN RUBBERY POLYPROPYLENE

By

Ying Qin

With the increasing usage of polymers as food and pharmaceutical packaging materials, more information is needed on the barrier properties of these packaging materials. The organic barrier property of polypropylene (PP) was studied in this project. A continuous gravimetric method was developed to study the sorbate uptake and sorption kinetics of benzaldehyde vapor in rubbery PP resin, sheet and polyhedron thermoformed container by using a SGA-100R gravimetric analyzer including Rubotherm magnetic suspension microbalance at 25°C, 0% RH. Solubility coefficients for benzaldehyde sorption in PP resin, sheet and container were determined based on the equilibrium uptake. Diffusion coefficients were also calculated on PP resin and sheet in the Fickian diffusion region. The experimental results demonstrated that the polymer conversion process had a great impact on the mass transfer properties of PP. The sorption of benzaldehyde in the PP polyhedron container was twice that of the sorption in PP sheet at lower vapor activities, and the sorption in sheet was almost three times the sorption of the resin at higher vapor activities. The sorption dynamics among the PP forms were different from each other. This finding emphasizes the need to assess mass transfer of formed polymer sheets or containers to accurately determine the barrier properties of packaging systems.

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Abbreviations and Symbols

atm	standard atmosphere, 1 atm=1.01*10 ⁵ Pascals
b	Langmuir affinity constant
cm	centimeter
С	concentration of permeant at the polymer interface
CD	concentration of permeant in Henry's law mode sorption
С _н	concentration of permeant in Langmuir mode sorption
С'н	Langmuir capacity constant
Cp	concentration of organic in the polymer at equilibrium
C _v	concentration of organic in the vapor at equilibrium
D	diffusion coefficient
D*	diffusion coefficient in an amorphous state
D_0	value of D at zero concentration
$D^{\mathbf{B}}{}_{\mathbf{A}}$	diffusion of vapor relative to stationary sheet
DPA	dew point analyzer
DSC	differential scanning calorimetry
D^{V}	mutual diffusion coefficient
$E_{ m app}$	apparent energy of activation for diffusion
E _D	activation energy of diffusion
Ep	apparent activation energy of permeation
EVOH	ethylene vinyl alcohol
F	rate of transfer

FDA	Food and Drug Administration
FFV	Fractional free volume
g	gram
GPC	gel permeation chromatography
in	Inch
Kg	kilogram
1	film thickness
li	bond distance between two atoms
Mt	sorbate uptake at time t
M_{∞}	sorbate uptake at equilibrium
mg	milligram
min	minute
mL	milliliter
mm	millimeter
Mn	number average molecular weight
mol	mole
Mw	weight average molecular weight
N _A	Avogadro's number
N ₂	nitrogen
R	universal gas constant
RH	relative humidity
р	partial pressure of penetrant
Р	permeance

Р	vapor pressure
<i>P</i> ₀	saturation vapor pressure
PP	polypropylene
ppm	parts per million
psi	pound per square in (1 psi = 6894.76 pascals)
QCM	quartz crystal microbalance
r _i	radius of atom I convalently bonded to A
RPM	pesolutions per minute
S	solubility coefficient
S*	solubility coefficient in an amorphous sate
sec	second
sp gr	specific gravity
STP	standard temperature and pressure
t	time
Т	absolute temperature
Tg	glass transition temperature
\mathbf{V}_1	volume fraction of the permeant in the polymer
VA	vapor activity
v _{sp}	specific volume
vw	Van der Waals volume
<i>v</i> ₀	occupied volume
Wt.	weight
μg	microgram

μl	microliter
$\Delta H_{\rm S}$	molar heat of sorption
Т	tortuosity factor
В	chain immobilization factor
ρ	density
ϕ_{a}	volume fractio of amorphous phase

CHAPTER 1. INTRODUCTION

GENERAL INTRODUCTION

The use of polymers as food and pharmaceutical packaging materials has experienced rapid and continuous growth in recent years. Polymer packages have evolved from simple monolayer structures to multilayer hybrid structures or from simple wraps to sophisticated containers which have additional demands placed on them. With the increasing usage of polymers as food and pharmaceutical packaging materials, more attention has been paid to the barrier properties of polymeric packaging materials (William, 1990). The interaction of polymer packaging materials with the environment and package contents has been the subject of increasing research and material development. New high barrier and biodegradable polymers are increasingly used in packaging applications (Hernandez, 1999, 2000; Lange, 2003) and thus there is a need to assess mass transfer phenomena of multiple organic compounds as applied to polymer and packaging science.

1.1 Mass Transfer

The mass transfer process between polymer and product and or environment is normally referred to as packaging interaction. Mass interactions in packaging systems develop from the moment the package and product come into contact during production, and extend throughout the package's shelf life. Packaging interactions include sorption, migration and permeation processes. In addition, chemical reactions (like oxidation) may develop as a consequence of these processes.

Sorption is the uptake of product components by the package material. The extent of a sorption process depends on the initial concentration of the sorbate in the product and the equilibrium thermodynamics between the plastic and product.

Migration is the transfer of substances originally present in the plastic material into a packaged product. These particular substances are called migrants, they could be residual monomers, solvents, remaining catalysts, and polymer additives. Migration may affect the product's sensory quality as well as its toxicological characteristics since it may incorporate into the food undesirable components from the package. The presence of potentially migrating substances in the packaging material is the object of intense legal control by the FDA and other regulatory agencies in other countries.

Permeation is the diffusion-controlled molecular exchange of gases, vapors or liquids (called permeant), across a homogeneous packaging material witch has no perforations or cracks. A permeation process may significantly alter the product's quality since the product may gain or lose components, and develop unwanted chemical reactions.

The migration of organic compounds of product into polymers is termed "sorption" or "scalping". Sorption is a factor that induces quality alteration during storage. The removal of desirable organic components from a product by plastic package materials has detrimental effects, such as change in the ingredient concentration thus changing medical function, or altering the flavor profile. Furthermore, sorption of organic components can compromise the package integrity or damage the package material by causing delamination of a multistructure or polymer swelling, thus leading to further sorption, and to a reduction in the shelf-life of the packaged product. Sorption of organic compounds is important to the packaging industry because it is an issue related to consumer safety and consumer acceptability of the packaged project. Therefore, the study of mass transfer, especially the solubility, diffusion and permeation of organic compounds through polymeric packaging structure has practical importance (Risch, 1991).

Disregarding obvious discontinuities such as cracks or pin holes in the material, permeants would be transferred through the packaging materials in a specific way depending on several factors: 1) The chemical structure of polymer and permeant, such as polarity of the permeating pair. The old rule of "like dissolves/permeates like" can be applied here. 2) Polymer morphology, such as free volume, orientation, tacticity, and crystallinity. Normally increasing crystallinity, density, polymer orientation and cross linking, decreases permeability. 3) The environmental conditions including temperature and relative humidity (RH). The change in permeability with temperature follows an Arrhenius equation within specific temperature ranges. Relative humidity may increase or decrease permeability depending on polymer and permeant type. For example, oxygen

permeability increases along with the increase of RH for EVOH and Nylon 6; however, oxygen permeability decreases with increase RH in amorphous nylon. 4) Finally the polymer processing and manufacturing, such as casting, injection blow molding or thermoforming, usually impact polymer morphology which will influence the mass transfer process.

1.2 Mass Transfer in Polymer Systems

The diffusive mass transfer, as observed in practical application of polymeric systems is normally categorized in two ways: permeation of simple gases (such as oxygen, carbon dioxide and water), or of organic vapors (such as flavor, additives, monomer, or solvents left in the polymer during polymer processing). The permeation of simple gases through thin layers of polymers is the most widely studied and the permeation rules are relatively simple. While the mass transfer of heavier organic vapors and liquids as occurred in polymeric constructions such as plastic containers and bottles is more complicated. Very often there is stronger interaction between penetrant and polymer, and between penetrant and penetrant.

1.2.1 Basic Concepts

The permeation process can be described as a three-step event. First, collision of the penetrant molecule with the polymer is followed by sorption in the polymer. Next, migration through the polymer matrix by diffusion, and finally, desorption of the permeant from the polymer completes the process. The fundamental driving force that prompts a molecular specie to transfer within the polymer, or between a polymer and a surrounding phase is, according to the solution theory, the tendency to equilibrate the species' chemical potential. For simple gases, a general relationship between the three main permeation properties permeability coefficient (P), solubility coefficient (S) and diffusion coefficient (D) is almost exactly valid:

$$P = S \cdot D \tag{1}$$

where P is the steady-state transport rate of permeant molecules through a polymer membrane of unit area per unit of thickness and driving force, while D is a kinetic parameter, which represents how fast the permeant molecules move through the polymer bulk phase. S is an equilibrium partition coefficient for distribution of the penetrant between polymer and vapor phase. For all three physical quantities P, S and D, the temperature dependence can be described by a Van't Hoff-Arrhenius equation (Krevelen, 1997):

$$S(T) = S_0 \exp(-\Delta H_s / RT)$$
 (2)

$$D(T) = D_0 \exp(-E_D / RT)$$
(3)

$$P(T) = P_0 \exp(-E_P / RT)$$
 (4)

where $\Delta H_{\rm S}$ = molar heat of sorption

 $E_{\rm D}$ = activation energy of diffusion

 $E_{\rm P}$ = apparent activation energy of permeation

As a sequence of equation (1), there are

$$P_0 = S_0 \bullet D_0 \tag{5}$$

$$E_P = \Delta H_S + E_D \tag{6}$$

Solubility coefficient (S) and diffusion coefficient (D) are usually determined by observing the weight change of a polymer sample during a sorption process by a gravimetric method. Diffusion coefficient (D) and permeability coefficient (P) values are obtained from permeability studies where the transport of a permeant through a polymer membrane is continually monitored (i.e., isostatic procedure) or by quantifying the amount of the penetrant that has passed through the film and accumulated as a function of time (i.e., quasi-isostatic procedure). By the gravimetric method, the equilibrium organic uptakes in sorption experiments are used to calculate the solubility coefficient (S). S is an equilibrium partition coefficient for distribution of the penetrant between polymer and vapor phase. It is a measure of the mass of permeant molecules sorbed by a unit of polymer mass per unit of partial pressure, and it is defined according to equation:

$$S = \frac{C_p}{C_v} \tag{7}$$

where C_p is the concentration of organic in the polymer at equilibrium (µg aroma/mg polymer), and C_v is the concentration of organic in the vapor at equilibrium (P/P_{sat}, ppm).

For the simplest case of more or less ideal permeation behavior, which includes polymers above their glass transition temperature and at low penetrant pressure, the relation between sorbate concentration and partial pressure can be described by the linear sorption isotherm Henry's law of solubility:

$$C = k_{\rm D} p \tag{8}$$

where C is concentration of diffusion permeant measured at the polymer interface, p is the partial pressure of penetrant at the contacting phase interface, and k_D is the proportionality constant of Henry's law. In fact, it is the solubility coefficient when there is no concentration dependence. In that case, S is the amount of substance (gas) per unit volume of solvent (polymer) in equilibrium with unit partial pressure. For simple gases S is usually given in cm³ (STP) / (cm³ polymer \cdot bar).

For the permeation of simple gases of low molecular weight in rubbery polymers and under relatively moderate pressures, the diffusion mechanism is Fickian and the departures from Henry's law for the sorption are negligible. The basic equations for describing the diffusion process are Fick's first and second laws of diffusion (Crank, 1975),

$$F = -D\frac{\partial C}{\partial x} \tag{9}$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{10}$$

where F denotes the rate of transfer, c is the concentration of diffusing substances, t is time, and x is the space coordinate. Then D is the mutual diffusion coefficient, in $(length)^2/time$. To obtain the flux (F) or the diffusion coefficient (D) from equations (9) and (10), initial and boundary conditions associated with the experimental method are needed, and the expressions would be solved (Hernandez, 1986a). Solution of Equation (10), associated with the initial and boundary conditions, can be performed numerically or analytically. In the latter case, a power-series of solutions usually arises when solving for the unsteady state case. Crank (1975) presented simplified equations related to the first approximation of the power series. It should be recognized that only approximate values will be obtained when the diffusion coefficient is calculated using these equations. More accurate estimation of this parameter can be carried out by using other methods; for example, a nonlinear maximum likelihood sequential method based on the Gauss linearization method (Beck, 1977). Alternative forms of Equation (10) for different co-ordinate systems such as may arise in considering diffusion in a cylinder or sphere are all included in the equation:

$$\frac{\partial C}{\partial t} = div(gradC). \tag{11}$$

1.2.2 Sorption Kinetics

1.2.2.1 Constant Diffusion Coefficient

The method in terms of the uptake of vapor by a plane sheet is based on the assumptions that the diffusion coefficient is constant and the sheet does not swell. The experimental procedure is to suspend a plane sheet of thickness *l* in an atmosphere of vapor maintained at constant temperature and pressure, and to observe the increase in weight of the sheet and hence the rate of uptake of vapor. The appropriate solution of the diffusion equation may be written

$$\frac{M_{l}}{M_{\infty}} = 1 - \frac{8}{\pi^{2}} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^{2}} \exp\left[\frac{-D(2m+1)^{2} \pi^{2} t}{l^{2}}\right]$$
(12)

if the uptake is considered to be a diffusion process controlled by a constant diffusion coefficient D (Crank, 1975). Here, where M_t is the total amount of vapor absorbed by the sheet at time t, and M_{∞} the equilibrium sorption attained theoretically after infinite time, l is the thickness of the film. The application of Equation (12) is based on the assumption that immediately the sheet is placed in the vapor the concentration at each surface attains a value corresponding to the equilibrium uptake for the vapor pressure existing, and remains constant afterwards. The sheet is considered to be initially free of vapor. $(t/l^2)_{1/2}$ represents the value of t/l^2 for which $M_t/M_{\infty} = 1/2$, is approximately given by

$$\left(\frac{t}{l^2}\right)_{\frac{1}{2}} = -\frac{1}{\pi^2 D} \ln\left\{\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right\}$$
(13)

the error being about 0.001 per cent. Thus we have

$$D = \frac{0.049}{(t/l^2)_{1/2}} \tag{14}$$

and so if the half-time of a sorption process is observed experimentally for a system in which the diffusion coefficient is constant, the value of this constant can be determined from Equation (14) (Crank, 1975).

1.2.2.2 Sorption by a Swelling Sheet

In deriving Equation (12) the thickness *l* of the sheet is assumed to remain constant as diffusion proceeds. In practice, sometimes, the sheet swells and the thickness increases as the vapor enters. Equation (12) can still be used in such cases, as suggested by Crank (1975) (p.207), by taking a frame of reference fixed with respect to the substance of the sheet, and concentration and thickness are measured. Thus the basic volume of the sheet is taken to be its volume in the absence of vapor and use the unit of length ζ_B such that unit ζ_B contains, per unit area, unit basic volume of the substance of the sheet B. Then the thickness of the sheet, measured in these units, is constant and equal to the original unswollen thickness, and the diffusion coefficient deduced from Equation (12) by substituting the original thickness for *l* is that for the diffusion of vapor relative to stationary sheet (denoted by D^B_A). If there is no over-all volume change on mixing, i.e. if the increase in volume of the sheet is equal to the volume of vapor sorbed at the vapor pressure existing in the experiment, the

coefficient obtained by this sorption method is related to the mutual diffusion coefficient D^{v} , deduced by the Matano procedure (Crank, 1975), by

$$D^{\rm B}_{\rm A} = D^{\rm V} (1 \text{-volume fraction of vapor})^2$$
 (15)

1.2.2.3 Concentration-dependent Diffusion Coefficient

Clearly from Equations (12) and (14) the value of t / l^2 for which M_t / M_{∞} has any given value, and in particular the value of $(t / l^2)_{1/2}$, is independent of M_{∞} when the diffusion coefficient is constant. However, Crank and Park (1949) showed a set of curves obtained experimentally for the uptake of chloroform by a polystyrene sheet, each curve corresponding to a different vapor pressure and hence a different M_{∞} . It was evident that $(t / l^2)_{1/2}$ decreased considerably the greater the value of the final uptake M_{∞} and therefore the diffusion coefficient was not constant but increases as the concentration of chloroform was increased. The problem was to deduce quantitatively how the diffusion coefficient is related to concentration, given the half-time of sorption experiments carried out for a number of different vapor pressures.

Application of Equation (14) to each sorption curve yields some mean value, \overline{D} , of the diffusion coefficient averaged over the range of concentration. Calculations by Crank (1968) have shown that for any one experiment \overline{D} provides a reasonable approximation

to $(1/C_0) \int_{0}^{C_0} Ddc$, where 0 to C_0 is the concentration range existing in the sheet during that experiment. By deducing values of \overline{D} from the initial gradients for each of a series of sorption experiments and using the approximate relationship

$$\overline{D} = (1/C_0) \int_0^{C_0} Ddc \tag{16}$$

a graph showing DC_0 as a function of C_0 can be drawn and numerical or graphical differentiation with respect to C_0 gives a first approximation to the relationship between D and C.

In many cases the first approximation is sufficiently accurate. If not, a method of obtaining successively better approximations is available (Crank, 1956), but in its most general form the calculations involved in evaluating successive approximations are lengthy.

In many polymer systems the diffusion coefficient depends approximately either linearly or exponentially on concentration and so, for these cases, correction curves have been produced by Crank (1956) showing the difference between $(1/C_0) \int_0^c Ddc$ and \overline{D}/D_0 , where D_0 is the value of D at zero concentration. Use of these curves usually removes the need for a second approximation.

1.2.3 Sorption Model

The term sorption represents the dissolution of the penetrant in the matrix polymer. This term includes in the absorption, the adsorption, and the trapping in microvoids or the clustering of aggregates. It is possible that diffusing molecules may be sorbed according to different sorption modes even in the same polymer membrane. Furthermore, the distribution of penetrant between different modes of sorption may change with changes in temperature, swelling-induced structural state, sorbed concentration, time, and other factors.

The equilibrium amount of penetrant sorbed and its sorption distribution mode, in a polymer under given conditions, are governed by the thermodynamics of the polymer-penetrant system, in particular by the nature and the force of the interactions. Basically there are five classic cases of sorption as shown in Figure 1.1 (Klopffer, 2001). The typical interaction associated with each mode was indicated by Klopffer (2001) as shown in Table 1.1. It is to be emphasized that sometimes it is likely that two or more modes of sorption will occur concurrently.



Figure 1.1 Typical isotherm plots of sorbed concentration vs. vapor pressure.

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Sorption mode	Main component interactions
Henry's law	polymer-polymer
Langmuir	polymer-penetrant
Dual mode	combination of Henry's and Langmuir modes
Flory-Huggins	penetrant-penetrant
BET	combination of Langmuir and Flory-Huggins modes

1.2.3.1 Henry's Law Sorption

The simplest case is that of ideal solution behavior with sorbed penetrant randomly dispersed within the polymer such that Henry's law is obeyed as follows:

$$C = S p \tag{17}$$

S is the Henry's law constant, which is the solubility coefficient. The solubility coefficient is then a constant independent of sorbed concentration at a given temperature. The sorption isotherm is a linear relationship of penetrant concentration versus partial pressure (or vapor activity), as showed in Figure 1. This mode is observed essentially for low pressures when the penetrant-penetrant and the penetrant-polymer interactions are weak as compared with the polymer-polymer interactions.

1.2.3.2 Langmuir Equation

In terms of the molecular pair distribution approach, this type represents a preference for polymer-penetrant pairs to be formed at relatively small pressures, with a smaller amount of sorption of more nearly ideal solution behavior at higher pressures. In physical terms, this represents initial sorption on some kinds of specific sites in the polymer, i.e. pre-existing microvoids or high-area inorganic fillers. When all the sites are occupied, a small quantity of diffusing penetrant may solubilise and dissolve in the polymer with a more or less random distribution according to the following:

$$c_H = \frac{C'_H bp}{1 + bp} \tag{18}$$

where C'_{H} is the Langmuir capacity constant [cm³(STP)/cm³] and b is the Langmuir affinity constant (atm⁻¹).

1.2.3.3 Dual-Mode Sorption

This model was initially proposed by Barrer (1958) to explain the concentration dependence of the solubility coefficient in glassy polymers, it was then extended by Paul and Koros (1976) for the diffusion coefficient. This mode describes the existence of two distinct populations of diffusing molecules (with local equilibrium between them). At the equilibrium pressure p, the concentration of the dissolved molecules in the polymer by an ordinary mechanism dissolution, C_D , obeys Henry's law (Equation 17), and the concentration of molecules sorbed in a limited number of pre-existing microcavities is given by the equation of Langmuir (Equation 18). In this situation, the sorption corresponds to the combination of the above two modes and is then given by this expression for sorption of non-permanent gases in glassy polymers:

$$C = C_{D} + C_{H} = Sp + \frac{C'_{H} bp}{1 + bp}$$
(19)

where the subscripts D and H represent Henry' law mode sorption and Langmuir mode sorption, respectively, and b is a constant, characterizing the affinity for the specific sites (microvoids or holes). The Equation 19 is a three parameter model, S, $C_{\rm H}$ and b, and is known as the dual-sorption isotherm or immobilized dual-sorption model. This model is valid for describing the curves observed in the case of sorption of low-activity gases in glassy polymers under moderate pressures, in the absence of strong interactions.

1.2.3.4 Flory-Huggins Mode

The Flory-Huggins mode isotherm represents the situation when the interactions between the diffusing molecules are stronger than the penetrant-polymer interactions and the solubility coefficient increases continuously with pressure. The sorption is then given by the Flory-Huggins equation:

$$\ln(P/P_0) = \ln(V_1) + (1 - V_1) + \chi(1 - V_1)^2$$
(20)

where P and P_0 are the vapor pressure and the saturation vapor pressure of the gas at the experimental temperature, individually; V_1 is the volume fraction of the permeant in the polymer and χ is the interaction parameter between the polymer and the solute.

Two principal physical interpretations of this behavior are possible: First molecules sorbed in the polymer tend to loosen the polymer structure locally and make it easier for subsequent molecules to enter in the neighborhood of the first than to go elsewhere. This interpretation implies the effective plasticization of the polymer by the sorbed penetrant. Type IV isotherms are observed when a liquid or vapor penetrant is a strong solvent or swelling agent for the polymer. Although polymer-penetrant interactions are relatively strong, they are not specific in the sense of site-penetrant interactions. Another physical interpretation of type IV behavior is reserved for systems in which penetrant-penetrant interactions. The strong penetrant-penetrant interaction causes the association of stable clusters or

aggregation of sorbed penetrant molecules, which would be relatively less mobile in comparison with isolated molecules. Hence, if the proportion of clustered molecules increases with increasing sorbed concentration C as implied by a type IV isotherm, then it would be expected that the diffusion coefficient D of the polymer-penetrant system would decrease with increasing C. This has been observed by Machin and Rogers (1972) in a number of water-polymer systems and contrasts with the behavior of sorbed solvents or swelling agents with D increases with C.

1.2.3.5 BET Equation

The last case corresponds to the combination of type Langmuir at low pressures and Flory-Huggins mode at higher pressures. Such isotherms frequently describe the sorption of water by the more hydrophilic polymers (Hernandez, 1992; 1994). Initially, water molecules are strongly sorbed in specific sites corresponding to the polar groups (usually hydroxyl, carboxyl or amide) in the polymer, then at higher relative vapor pressures solution or clustering processes may predominate.

The above physical interpretations are probably oversimplified. In particular, it is likely that two or more models of sorption will occur concurrently. So far no information on the degree of overlap of the two modes can be deduced from the simple molecular pair distribution treatment.

1.2.4 Fickian and Non-Fickian Characteristics

A sorption curve is a plot of the amount of vapor M_t absorbed in or desorbed (in grams) from unit gram or cubic centimeter of dry polymer as a function of the square root of time t. The distribution of a diffusant during sorption is governed by the one-dimensional differential equation for diffusion presented by Fick, with the space co-ordinate taken in the direction of the film thickness. Solutions appropriate to the initial condition of the sorption experiment (i.e., at t = 0 the concentration is uniform in the film) were obtained by Crank (1956), subject to the assumptions that D is a function of concentration C only and that when the ambient pressure is changed from an initial value p_i to a final value p_f the concentrations at the surfaces of the film instantaneously increase or decrease to the equilibrium value C_f corresponding to p_f . Sorption curves having characteristics expected from the above-mentioned assumptions for D and the surface concentration are customarily called *Fickian* or *normal* type. At the molecular level, the essential conditions for Fickian sorption are associated with a high mobility of polymer segmental units.

The important Fickian sorption features indicated by Crank (1968) include: Both absorption and desorption curves are linear in the initial stage. For absorption, the linear region extends over 60% or more of M_{∞} ; Above the linear portions the sorption curves are concave to the abscissa, irrespective of the form of D(c); For absorptions from a fixed C_i to different C_f 's, the initial slope of the reduced curve becomes larger as the concentration increment $C_f - C_i$ becomes larger, provided that D increases monotonically with C in the
range considered. These are characteristic features of such so-called 'Fickian' behavior. Systems which show deviations from this behavior have been termed 'non-Fickian' or anomalous. The calculation of diffusion coefficients for the latter systems must account for the concurrent relaxation processes with appropriate caution in subsequent interpretation of the results.

1.2.4.1 Sorption Well Above T_g

Previous work demonstrated that sorption and permeation, which are typical diffusion-controlled processes, of organic vapors in polymer solids exhibit different features in the regions above and below the glass transition temperature, T_g , of a given polymer. Normally they are rather simple at temperatures above T_g and exceedingly complex at temperature below T_g (Crank, 1968).

At temperatures well above T_g , the polymer is in the rubbery condition. Various models developed to describe the diffusion of small gas molecules in polymers generally fall into two categories: molecular models and free volume models (Stern, 1990).

Molecular models analyze specific penetrant and chain motions together with the pertinent intermolecular forces based on the energy considerations. Barrer (1937) first showed that the diffusion of molecules in polymers was a thermally activated process. Molecular models commonly assume that fluctuating microcavities or holes exist in the

polymer matrix and at equilibrium, a definite size distribution of such holes is established on a time-average basis. A hole of sufficient size may contain a dissolved penetrant molecule, which can jump into a neighboring hole once it acquires sufficient energy. A net diffusive flux arises in a preferred direction in response to a driving force; otherwise molecules will diffuse in random directions since their motion has a Brownian nature. The flux magnitude depends on the concentration of holes which are large enough to accommodate a penetrant molecule. Molecular models include these characteristics largely to describe the Arrhenius behavior of diffusion coefficients observed experimentally, i.e.

$$D = D_0 \exp(-E_{ann} / RT) \tag{21}$$

where E_{app} is the apparent energy of activation for diffusion, D_0 is a constant, R is the universal gas constant, and T is the absolute temperature. A correlation is found between E_{app} and the molecular diameter of the penetrant, but no theoretical expression for D has been obtained with molecular models.

Free volume models attempt to elucidate the relationship between the diffusion coefficient and the free volume of the system, without consideration of a microscopic description. One of the most promising and earliest free volume models was developed by Fujita (1960). Fujita suggested the molecular transport is due to redistribution of free volume and not due to a thermal activation. The free volume models argue that the total free volume is a sum of two contributions. One arises from molecular vibrations and cannot

be redistributed without a large energy change and the second is in the form of discontinuous voids. Diffusion in such a liquid is not due to a thermal activation process, but is assumed to result from a redistribution of free-volume voids caused by random fluctuations in local density (Stern, 1990). The basic idea of this theory is that a diffusing molecule can only move from one position to another when, in its neighbourhood, the local free volume exceeds a certain critical value. Based on this theory, the dependence of D with parameters such as the concentration, the penetrant shape and size, the temperature and the glass transition temperature of the polymer can thus be explained.

1.2.4.2 Sorption Below T_g

When the polymers are at temperatures below the glass transition temperature T_g , the polymer is in the glassy state. As indicated by Stern (1990), the difference in the mechanism is reflected in the significant differences observed in the dependence of the diffusion coefficient, as well as the permeability and solubility coefficients, on the penetrant gas pressure or concentration in polymers and on the temperature. A polymer in the glassy state has a specific volume V_s bigger than the specific volume of equilibrium V_1 . This difference, due to the non-equilibrium character of the glassy state, is at the origin of the non-linearity of the sorption isotherm (Barrer, 1958) that is the dependence of the solubility coefficient on pressure.

The difference in the transport and solution behavior of gases in rubbery and glassy polymer is due to the fact that the glassy polymers are not in a state of true thermodynamic equilibrium. Glassy polymers have very long relaxation times. Therefore, the motions of whole polymer chains or portions thereof are not sufficiently rapid to completely homogenize the penetrant's environment. Penetrant molecules can thus potentially sit in holes or irregular cavities with very different intrinsic diffusional mobilities (Frisch, 1980). Thus it is possible that there are more than one mode of penetrant absorption and diffusion in glassy polymers exist (Stern, 1990). The dual mode sorption model (Barrer, 1958) is the most usually used model to describe the solution and the diffusion of molecules in glassy polymers. The gas-polymer matrix model was developed by Sefcik (1983) and Raucher (1983) to express the dependence on concentration of sorption and gas transport phenomena in glassy polymers.

1.2.5 Temperature and Concentration Dependence

When the diffusant component has a molecular size much smaller than the monomer unit of a given polymer and the thermodynamic interaction between the two components is very weak, a limited rotational oscillation of only one or two monomer units would be sufficient to give a cross-section for the diffusant molecule to jump thermally from one position to a neighboring one. The diffusion of simple gases, such as hydrogen, argon, nitrogen and carbon dioxide, in ordinary polymer substances and of water in hydrophobic polymers probably involves such a molecular mechanism. Molecules comparable with, or larger than, the monomer unit of a polymer require for their diffusion that a co-operative movement by the micro-Brownian motion of several monomer units, i.e. the so-called polymer segment, take place. Such substances include most organic vapors, which are either solvents or swelling agents for ordinary polymers. Many features of their diffusion reflect the micro-Brownian motion of long-chain molecules and thus are unique to polymer systems (Crank, 1968).

The rate of diffusion of an organic vapor in a polymer solid is found to be primarily controlled by the mobility of the polymer segmental unit. The polymer chain segmental motion is mainly affected by two factors, temperature and concentration of sorbed penetrant within the polymer. The diffusion coefficients of polymer-organic vapor systems generally increase with increasing diffusant concentration and temperature.

It is believed that raising the temperature provides energy for a general increase in segmental motion. If the energy density is sufficient, the polymer may pass through structural transitions, such as the glass and melting transitions, which further affect the solution and diffusion process (Rogers, 1985). The effects of an increase in temperature may also enhance the micro-Brownian motion of segmental units and expands the system (increase in free volume), thus the average inter-chain distance is increased and the molecular interaction between neighboring polymer molecules is weakened (Fujita, 1968).

The presence of sorbed penetrant also increases the free volume of the system. If the solution process is ideal, with no volume change on mixing, the change in system free volume with increasing concentration will be proportional to that obtained by an increase in temperature. However, concentration dependence may differ from the temperature due to the possibility of specific component interactions, i.e. modes of sorption, which affect component mobilities and the relative free volume contribution to the mixture by components involved in different modes of sorption (Rogers, 1985).

1.2.6 Effect of Polymer Relaxation

It should also be considered that the ease with which the diffusant molecule can jump by thermal agitations from one position to its neighbor in a polymer may also depend on the physical details at those positions. As postulated by Crank and Park (1951), when a polymer substance absorbs a vapor, the internal stresses may be set up and the polymer molecules rearrange themselves toward a new equilibrium conformation consistent with the sorbed state. This conformational change, however, may not take place instantaneously. Thus the instantaneous conformation of a polymer chain in any given volume element during a sorption process generally differs from the one when the chain was equilibrated with the particular concentration. Thus it indicates that the chain conformation is a volume element as not uniquely determined by the diffusant concentration there, but may depend on the time taken by the element to reach that particular concentration.

When a polymer substance absorbs a vapor, the internal stresses may be set up and the polymer molecules rearrange themselves toward a new equilibrium conformation consistent with the sorbed state. It is to be expected the inner, unswollen (or less swelling) part of the solid will exert a compression force on the outer, swelling part, while the swollen part will exert a force on the unattached region that tends to expand the solid. These compression and expansion forces change as sorption proceeds, since the concentration distribution in the solid changes with time and since the polymer chains tend to relieve these stresses by changing their conformations. Thus if the internal stresses do affect the process of diffusion, it allows D to be time-dependent (Crank, 1951).

However, at temperatures well above T_g the micro-Brownian motion of polymer molecules is sufficiently active even in the undiluted state of a given polymer to enable equilibrium to be reached rapidly. Therefore, at such temperatures, the chains in any volume element of the polymer may take up almost instantaneously an equilibrium conformation consistent with the sorbed state when a vapor diffuses into the solid. With the micro-Brownian motion of polymer chains being sufficiently active, the time-dependence of *D* due to internal stress should disappear, since the stress set up by swelling immediately decays by a rapid chain relaxation. In this way we can understand that at temperatures well above T_g the diffusion coefficient of a polymer-organic vapor system becomes free from any time-dependent effect and depends only on the diffusant concentration (Fujita, 1968). This is so called 'Fickian' behavior. The purely concentration-dependent D is sometimes called the equilibrium diffusion coefficient, since it is associated with the equilibrium chain conformation.

In comparison, sorption and transport in polymers with long relaxation times often exhibit features which cannot be described adequately by any generalized form of Fick's law with constant boundary conditions and with the diffusion coefficient dependent only on concentration. This so-called 'non-Fickian' behavior usually occurs with glassy polymers, with semicrystalline polymers above T_g , and with polymers with more rigid chain conformations and higher internal viscosity when the penetrant swells the polymer. In such cases, *D* may be a function of concentration, time, the spatial coordinates and history of the sample. The boundary conditions for diffusion depend on time and other variables such that the surface concentrations change with time, applied stress, etc (Rogers, 1985).

The type of behavior is characterized experimentally by the concentration gradient profile during sorption and its time dependence. The time dependence is conveniently determined by the slope n of a plot of log M against log time, where M is the amount of penetrant sorbed. In a sheet geometry, Fickian sorption has n = 1/2. Sorption with n between 1/2 and 1 is non-Fickian diffusion (Rogers, 1985)

The relaxation times in polymers are related to the many modes of relaxation. All relaxation times decrease with increasing temperature or concentration, with some decreasing more rapidly than others. Rogers (1985) believed that the overall sorption process reflects those relaxation motions of the polymeric matrix which occur on a time scale comparable to or greater than the time scale of the concurrent diffusion process.

1.3 Parameters Affecting the Transport Properties

The barrier properties of polymeric materials are determined by the chemical structure of the chain and the polymer morphology. The parameters derived from chemical structure, such as degree of polarity, intermolecular forces, ability to crystallize and chain stiffness, are essentially determined upon the selection of the particular polymer. Generally, orientation and crystallization of polymers improves the barrier properties of the material as a result of the increased packaging efficiency of the polymer chains.

As postulated by Michaels *et al.* (Michaels, 1959; Michaels and Bixler, 1961a, b), the concept that the sorption and diffusion took place exclusively in the amorphous regions has been widely accepted. The crystalline zones act as excluded volumes for the sorption process and are impermeable barriers for the diffusion process. The dispersed crystalline phase presents a resistance to the permeant passage. Moreover, their existence does not seem to influence the sorption mode in the amorphous phase. More exactly, Klopffer

(2001) indicated that these crystalline zones have two effects on gas diffusion. On one hand, they increase the effective path length of diffusion; and on the other hand, they seem to reduce the polymer chains mobility in the amorphous phase because the chain ends are trapped in the neighbouring crystalline lamellae, and then lend to a higher activation energy of diffusion. Michaels *et al* (1959, 1961a,b) thus introduced a "tortuosity factor" τ and a "chain immobilization factor" β to account for these effects.

They proposed the following expressions for the coefficients of solubility and diffusion:

$$S = S * \phi_a \tag{22}$$

$$D = \frac{D^*}{\beta\tau}$$
(23)

where S^* and D^* are the coefficients of solubility and diffusion in an amorphous, hypothetical, completely relaxed state (*i.e.* a completely amorphous polymer), and ϕ_a , the volume fraction of amorphous phase. β , the factor relating to chain immobilization, reflects the hindrance of the crystalline zones on the amorphous zone. The tortuosity factor τ , characterizes the more tortuous pathway that a diffusing molecule must take in a semicrystalline zones. It is a geometrical term which depends on the crystallites anisotropy degree, the degree of crystallinity and hence, the thermal history. For a constant volume fraction of amorphous phase, β is correlated to temperature by an exponential relation whereas τ is constant. β and D^* are both supposed to depend on the penetrant diameter (Klopffer, 2001). Certain evidence has shown that the crystalline phase affects the nature of the amorphous phase (Michaels and Bixler, 1961b). More recent studies (Puleo, 1988; Mogri and Paul, 2001; Weinkauf, 1990) have shown that certain crystalline structures will permit small molecule sorption and diffusion. The results can be explained by a more open structure of these crystals with a density not very different from that of the amorphous phase. Recently, it was also shown that molecules could penetrate into crystals of δ form in syndiotactic polystyrene (Guadagno, 1998; Manfredi, 1997).

In the case of amorphous or semicrystalline polymers, the coefficients S and D can be related to the free volume (V_f), which is defined as a space which is not occupied by the macromolecules and its value is equal to a difference between the specific and the occupied volumes of the polymeric system (Danch, 2003). Fractional free volume, FFV [cm³ of free volume/cm³ of polymer] is commonly used to characterize the efficiency of chain packing and the amount of free space available for gas permeation in a polymer matrix (Pixton, 1994; Bondar, 1999; Raharjo, 2005):

$$FFV = \frac{v_{SP} - v_O}{v_{SP}} \approx \frac{1/\rho - 1.3v_W}{1/\rho}$$
 (24)

where v_{sp} is the polymer specific volume, and v_o is the occupied volume of the polymer. The occupied volume is typically estimated as 1.3 times the van der Waals volume (v_w), which is calculated using group contribution methods (Krevelen, 1997). For an approximate calculation, the Van der Waals volume is assumed to be bounded by the outer surface of a number if interpenetrating spheres. The radii of the spheres are assumed to be (constant) atomic radii for the elements involved and the distances between the centers of the spheres are the (constant) bond distance. The contribution of a given atom A with radius R to the Van der Waals volume is then given by:

$$v_{W,A} = N_A \left[\frac{4}{3} \pi R^3 - \sum \pi h_i^2 (R - \frac{h_i}{3}) \right]$$
(25)
$$h_i = R - \frac{l_i}{2} - \frac{R^2}{2l_i} + \frac{r_i^2}{2l_i}$$
(26)

where N_A is Avogadro's number, r_i is the radius of atom i covalently bonded to A, and l_i is the bond distance between the atom A and i (Krevelen, 1997).

1.4 Methods for Studying the Sorption of Organics on Polymer Materials

Mass transfer of inert gases and water vapor has been well investigated and standardized methods are available for determining transmission rates for these permeants (ASTM E96-66, ASTM D3985-81) (Hernandez, 1986a). In contrast, current knowledge on mass transfer of organic substances is still limited and no standard procedures are available to determine the numerical values of these parameters (Hernandez, 1986a; Zhou, 2004). This is mainly due to the fact that organic substances are capable of interacting with the polymer matrix, leading to swelling of the polymer matrix, resulting in configurational changes and alteration of polymer chain conformational mobility and thus of penetrant diffusivity and permeability. Thus, for penetrants such as organic vapors which can exhibit physicochemical interactions with a polymer matrix, the solubility coefficient (S), diffusion coefficient (D), and permeability coefficient (P) should be determined experimentally in order to describe accurately the mass transfer behavior of penetrant / barrier systems involving organic vapors.

Study of the sorption of organics can be categorized to two branches: by polymer film / sheet, which is the most popular way researchers are adopting, and by container systems. Currently several methods have been used for measuring the mass transfer characteristics of polymer films or sheets, including isostatic permeation procedure (Zhou, 2004; Gavara,1996; Van Willige, 2002; Huang,1998), quasi-isostatic permeability method (Gavara,1996; Sajiki,1993); Hernandez,1986), thermal stripping / thermal desorption (TS/TD) procedure (Nielsent, 1994) and gravimetric technique (Baner,1986; Nielsent,1994; Barr, 2000), *etc.*

The studies of mass transfer in container systems were only reported by using sorption cell methods where the permeant was dissolved or suspended in a liquid and brought into contact with polymer (Safa,1999; Demertzis,1997). In that case, components such as aqueous media, or solvents used to disperse organic compounds may affect the partitioning. Among these methods, the gravimetric approach is very suitable and classic for the determination of solubility coefficient (S). The advantages of the gravimetric method are not only the simplicity in the manipulation of the polymer sample, but also continuously recording the weight gain by the test specimen as a function of time. The gravimetric method permits accurate and direct measure of the sorbate uptake at both transient (M_i) and steady state (M_{∞}). The M_{∞} value obtained at steady state can be used to

calculate S and M_t and M_{∞} values can be used to calculate D (Nielsent, 1994; Barr, 2000).

So far, several models of balance used in the gravimetric study of the sorption have been reported, such as Cahn 2000 suspension electrobalance (Barr,2000; Berens, 1989; McDowell, 1999), quartz crystal microbalance (QCM) (Oliverira, 2004), Rubotherm magnetic suspension balance (Kiparissides, 2003; Krüger, 2005), quartz-spring balance (Krüger, 2005), McBain spring balance (Dhoot, 2001), or Ohaus analytical plus electronic balance (Palamara, 2005).

The main difficulty of using conventional gravimetric instruments is the direct connection of the measuring cell (sample atmosphere) and the weighing instrument. The balance can be damaged or disturbed by the measuring atmosphere and the measuring atmosphere can be adversely affected by flushing gases and pollution. Another limitation of those conventional gravimetric instruments is the limitation on the sample shape and size, which are determined by the size of the chamber in the balance. Normally only a small amount of sample in the shape of powder, pellet or film could be tested. A SGA-100R gravimetric analyzer that includes a Rubotherm microbalance has been modified to make it possible to weigh samples contactlessly under nearly all environments and to facilitate the test on large sample, such as a container (Qin, 2005). This instrument was used in this project.

1.5 Mass Transfer Studies on Polypropylene

Several experimental techniques have been developed to measure gas transport in polyolefins at high pressures, especially polypropylene (PP) and polyethylene (PE). PP is a commodity polymer produced on a 10 billion pound per year scale in North America alone (Palamara, 2005). Sato (1999) measured Henry's constants for carbon dioxide and nitrogen in molten PP. Sato (2001) studied the solubility of propylene in semicrystalline PP. Tsuboi (2001) reported infinitely dilute partition coefficients for ethylene and propylene in semicrystalline PP. Sliepcevich (2000) used packed bed inverse gas chromatography to obtain partition and diffusion coefficients for ethylene and propylene in semicrystalline PP beads. Sorption of various organic solvents in atactic PP and isotactic PP was studied by Ochiai (1971) by using a quartz-spring balance. Palamara (2005) studied the diffusion and solubility of propylene and ethylene in atactic PP with the static sorption technique. The permeation of oxygen, water and limonene through printed and unprinted oriented PP films were studied and compared by Rubino (2001). Although many experimental techniques have been developed to measure mass transfer in polymers, experimental diffusivity and solubility data are still in short supply for many PP-organic systems, such as PP-benzaldehyde.

1.6 Objectives of the Project

Much of the current permeability data of organic compounds has been obtained only for flat films or sheets, and these values are then used to calculate the barrier properties of containers (Hernandez, 1992; Thalmann, 1990; Nir, 1996). In general, the forming process of a polymer such as blow molding, injection blow molding, thermoforming, by which containers are produced, changes the polymer structure and morphology. It induces localized effect and stresses in the final container that may produce variations in the barrier properties of containers compared with film or sheet (Jasse, 1994; Demertzis, 1997). Therefore, there are substantial differences in the barrier properties between containers and unformed polymer sheets. Using the permeability data generated from films and sheets for containers will cause some error in the prediction of the container barrier properties.

In this project, polypropylene sheets were manufactured and container shapes were produced by casting and thermoforming procedures, individually (Figure 1.2). The goal was to develop a method to study the sorption of organic vapor in polymers. The SGA100 R gravimetric analyzer was adopted in the study due to the long-term stability and high accuracy benefited from the separation of the balance magnet from the measuring cell. The sorption study was applied on PP resin, sheet and container shape. The correlation between sorption of organic compound and package configurations was studied. The effect of the manufacturing of polymer on sorption was also addressed.

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Figure 1.2. Schematic plan of the PP processing in this project.

The specific objectives for this project are:

- To develop a continuous gravimetric method to study the sorption of benzaldehyde vapor in polypropylene *via* Rubotherm magnetic suspension microbalance
- To demonstrate the impact of manufacturing on the sorption of benzaldehyde by comparing the sorption of resin, sheet and container
- To demonstrate the impact of morphology on the sorption of benzaldehyde on resin, sheet, container and atatic PP.

CHAPTER 2. MATERIALS, INSTRUMENT AND METHODS

2.1 Materials

2.1.1 Organic Sorbate

Benzaldehyde, purified by redistillation, \geq 99.5%, was obtained from Sigma-Aldrich Inc. (St. Louis, MO) and adopted as sorbate / permeant in this study. Benzaldehyde has been well identified as a natural flavor compound. It is the character impact flavor for cherry and almonds. It also helps give coffee and cocoa their characteristically pleasant aromas. Benzaldehyde is also widely used in the chemical industry, especially as starting material. Besides, benzaldehyde is safe and remarkably cheap—about 30¢ an ounce at chemical supply houses.

Benzaldehyde is easily oxidized. The oxidized product is benzoic acid in white solid. Benzaldehyde is also slightly sensitive to light and moisture. The operation of this liquid should be in the inert protection environment and avoid the long time light exposure (Wiberg, 1955; Hurd, 1929; .Potineni, 2005).

2.1.2 Polymer

Polypropylene (PP) resin pellets were used as the starting material in this study. PP resin was obtained from ExxonMobil chemical company (Huston, TX). It is a homopolymer produced with a Ziegler-Natta type catalyst in series bulk stirred tank reactors. It has density of 0.900 g/cm³ and total amount of additives less than 0.3 wt.%.

The molecular weight of PP resin by gel permeation chromatography (GPC) has been measured as an Mn of 60,000 g/mol and Mw of 250,000 g/mol, and an Mw/Mn ratio of 4.2. The resin has melt flow rate of between 2.5-3.1 g/10 min and an average degree of crystallinity of 39.4 % as determined by differential scanning calorimetry (DSC). The melting point measured by DSC was about 164.9 °C.

Atatic polypropylene (PP), a totally amorphous waxy solid with specific gravity 0.85 g/cm^3 and Mw of 12,000 g/mol, was obtained from Scientific Polymer products, Inc. (Ontario, NY).

Polypropylene was chosen because it is a commodity polymer and has been commercialized in the market for long time. PP is not a very good organic barrier, but it is useful for demonstrating the correlation between configuration and sorption behavior of a PP container shape in limited time range under the selected conditions.

2.2 Polymer Processing

2.2.1 Casting PP Sheet

Polypropylene resin pellets were considered as the starting material in this study. It was then formed to PP sheets in the thickness about 0.46 mm (~ 18 mil) and width of 15 cm (~ 6 in) by extrusion and casting from PP resin by a Killion KLB100 extruder (Killion Extruder Inc., Cedar Grove, NJ). Casting film is normally homogenous in thickness. The setting of the extruder was:

Temp. of zone 1^{st} to zone 3^{rd}	530 °F
Temp. of zone 4 th (die)	540 °F
Melt temp.	486 °F
Motor speed	112 RPM
Chill roller temp.	100 °F
Chill roller speed	0.86 RPM
Die gap	1.79 mm (70 mil)

2.2.2 Thermoforming PP Containers

PP polyhedron container shape with surface area (36.3 cm²) was designed. The polyhedron shape represented those containers that have lots of corners and edges. A male mold were chosen for producing the container shape over female mold because male mold can produce shapes with smaller thickness variance, thus improving the thickness uniformity. The mold was designed usingy Rhino software, it is shown in Figure 2.1 left; the thermoformed polyhedron container shape is shown in Figure 2.1 right. The polypropylene container shape was thus thermoformed on a Hydro-Trim 1620 thermoformer (Hydro-Trim Corp., West Nyak, NY) using the male mold. The setting of the thermoformer is:

Heating time	40 sec
Forming time	25 sec
Top temp. controller	410 °F
Bottom temp. controller	410 °F



Figure 2.1. Male mold (left) and thermoformed polyhedron shape (right).

2.3 Instrument

2.3.1 SGA-100R Gravimetric Analyzer

Sorption studies were conducted on SGA-100R gravimetric analyzer including Rubotherm magnetic suspension electrobalance (VTI Corporation, Scientific Instruments, Hialeah, Florida) by the continuous flow method (Hernandez, 1986b; Nielsent, 1994). The balance is optimized to have up to 10 g capacity with 1 µg resolution and it has been designed with a chamber in the dimension of 7.5cm×7.5cm×14cm (L×W×H), which is large enough to hold a whole plastic container. The vapor activity (VA) / relative humidity (RH) can be generated and constantly maintained. Because there are three vapor generators in this system, it is possible to produce mixed sorption conditions. The balance is designed to have long-term stability and high accuracy due to the separation of the balance magne and the measuring cell. The detailed instrument information is available in Chapter 3.

2.3.2 **Operation Procedure**

Prior to the sorption tests, the polymer sample, either PP resin pellets (approximately 120 mg), or a PP sheet sample in the dimension of 1" Length x 0.75" Width x 0.02" Thickness, or a PP polyhedron container shape was dried by a vacuum oven (40 °C, 30 in vacuum Hg) for 10 hours. After drying the sample was placed on the microbalance basket/hook within the chamber. A complete sorption experiment consisted of a series of runs including the specified conditions for sample drying (optional) and a sequence of vapor activities / relative humidities to which the sample was exposed. Vapor sorption was measured by continuously recording the weight uptake of the dry sample. In this study, the pre-dried sample was purged by N₂ for 2 hours in the balance chamber in the drying cycle. Five vapor activities (0.1, 0.3, 0.5, 0.7 and 0.9) were tested in the sorption study.

2.3.3 Differential Scanning Calorimetry (DSC) Analysis

TA instrument DSC Q100 was used in this project. DSC was adopted to determine the glass transition temperature (T_g), melting point temperature (T_m) and the heat of melting (ΔH), thus % crystallinity of polymer material. The DSC conditions were as follows: The method used was heat/cool/heat; N₂ carrier gas at 50 ml/min. The temperature was first raised at a rate of 20 °C/min to 200 °C and followed by cooling at a rate of 5 °C/min to -80 °C. It was then raised at a rate of 20 °C/min to 200 °C.

2.3.4 Gas chromatography (GC)

The composition of the vapor stream generated by gravimetric system was monitored by using GC (HP 6890 series) equipped with a gas flame ionization detector (FID), interfaced with an integrator. The GC conditions were as follows: The column was HP-5; H_e carrier gas at 2.2 ml/min; H₂ at 30 ml/min; air flow at 300 ml/min; N₂ at 25 ml/min; initial oven temperature, 40 °C for 5 min; temperature was raised at a rate of 20 °C/min to 140 °C and kept at this temperature for 1 min. The retention time for benzaldehyde is at 8.49 min. The calibration samples were prepared by putting 10 ml of benzaldehyde in a 40 ml hermetic vial under nitrogen atmosphere at 40 °C for 3 hours. Samples in the vial headspace (10-70 μ l) were injected into the GC port. The calibration curve was thus constructed by plotting the instrument response (area) vs. sorbate quantity (mol).

2.3.5 Polymer Density Test

The test procedure followed was in accordance with the ASTM D792-98 "Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement".

Specific gravity (relative density) is the ratio of the mass of a unit volume of the impermeable portion of the material in air at 23 °C to the mass of equal density of an equal volume of gas-free distilled water in air at the same temperature. Density is the mass in air in kilograms per cubic meter of impermeable portion of the material at 23 °C. Specific gravity can be converted to density by use of the following equation:

 $D^{23^{\circ}C}$, kg/m³ = sp gr 23/23 °C * 997.6

Test Procedure A (for testing solid plastics in water, specimens 1 to 50g) was adopted in this project. First, the test sample was conditioned at 23 °C \pm 2 °C and 50 \pm 5 % relative humidity for not less than 40 h prior to test. Second, the water temperature was measured and the sample was weighed in air as *a*. Third, the immersion vessel was mounted on the support, and the suspended sample and sinkers were completely immersed in water at a temperature of 23 °C \pm 2 °C. The vessel must not touch wire or specimen. Any bubbles adhering to the object were removed. The mass of the suspended sample was determined as *b* (the mass of the specimen, sinker and the partially immersed wire in liquid). Fourth, the wire and sinker were weighed in water with immersion to the same depth as used in the previous step, this weight was recorded as *w* (mass of the wire in liquid). The procedure was repeated for each sample. Three samples per type of polymer configuration were measured. The specific gravity of the plastics was calculated as follows:

Sp gr 23/23 °C = a / (a + w - b)

The density of the plastic can thus be calculated as follows:

 $D^{23^{\circ}C}$, kg/m³ = sp gr 23/23 °C * 997.6

In summary, the mass of the solid plastic sample was determined in air. It was then immersed in a liquid, its apparent mass upon immersion was determined, and its specific gravity (relative density) was calculated. The polymer characteristics by DSC and polymer density test are shown in Table 2.1:

	PP resin	PP sheet	PP polyhedron container
T _g , °C	-6.41	-6.13	-7.42
T _m , °C	164.9	160.8	166.7
Crystallinity, %	39.4	40.5	42.3
Density, g/cm ³	0.90*	0.87	0.85

Table 2.1. Polymer characteristics for different PP forms

* Obtained from Exxonmobil Chemical Company (Houston, Texas)

CHAPTER 3

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Measurement of Sorption of Benzaldehyde in Polymer with Magnetic

Suspension Electrobalance

This chapter is preparing for the submission to Polymer Testing in the section of Equipment and Test method.

Measurement of sorption of benzaldehyde in polymer with magnetic suspension electrobalance

Abstract

A new gravimetric analyzer including a magnetic suspension microbalance was set up and a method was developed to study the sorption of organic and/or moisture in polymer by a continuous gravimetric method. The balance has up to 10 g capacity with 1 µg resolution, and a large chamber with dimension of 7.5 cm×1.4 cm (L×W×H). The separation of the balance magnetic and the sample chamber improved the balance stability and accuracy. The gravimetric instrument was calibrated and the noise was quantified before the sorption study. The balance was used to evaluate the sorption of benzaldehyde vapor in polypropylene (PP). The sorption of benzaldehyde in rubbery PP resin exhibited Fickian sorption kinetics at low vapor activities (0.1-0.5) and a two-stage sorption incorporated both Fickian diffusion at the initial sorption stage and protracted polymer relaxation controlled mass uptake kinetics at high vapor activities (0.7-0.9). The sorption behavior of benzaldehyde in different PP forms (resin, sheet and container) was compared.

Keywords: gravimetric, sorption, benzaldehyde, polypropylene

3.1. Introduction

Mass transfer properties have been applied in gas separation membrane industry (Kesting, 1993), in which the economics is largely determined by the membrane's transport properties - permeability and selectivity for a specific gas in a mixture. In addition, there is an application of the mass transfer and sorption in packaging industry (William, 1990; Risch, 1991), in which high moisture, gas or organic barrier properties of polymeric packaging materials are always expected.

Several methods have been used for measuring the mass transfer characteristics of polymer films, including isostatic permeation procedure (Gavara, 1996; Huang, 1998), quasi-isostatic permeability method (Gavara, 1996; Hernandez, 1986 b), thermal stripping / thermal desorption (TS/TD) procedure (Nielsent, 1994) and gravimetric technique (Barr, 2000; Krüger, 2005). Among them, the gravimetric method was frequently used in the direct determination of permeant solubility and diffusion coefficients. The advantages of gravimetric method are due to its simplicity on the polymer sample manipulation and the continuously recording of the weight gain by the test polymer as a function of time or vapor activity. The gravimetric method permits accurate and direct measure of the sorbate uptake at both transient (M_1) and steady state (M_∞). The M_∞ value obtained at steady state can be used to calculate solubility coefficient (S) (Nielsent, 1994; Barr, 2000).

Several gravimetric instruments with different balance system have been used to carry out gravimetric study on polymer materials for the determination of sorption of different organic compounds or moisture, such as Cahn 2000 electrobalance (Barr, 2000; Berens, 1989; McDowell, 1999), quartz crystal microbalance (QCM) (Oliverira, 2004), Rubotherm magnetic suspension electrobalance (Kiparissides, 2003; Krüger, 2005), quartz-spring balance (Ochiai, 1971), McBain spring balance (Dhoot, 2001), and Ohaus analytical plus electronic balance (Palamara, 2005). Some of these gravimetric systems were incorporated with vacuum pump for polymer degassing and penetrant removal (Berens, 1989; Dhoot, 2001).

The main difficulties in using some of the gravimetric instruments consist in the direct connection of the sample atmosphere (sample in the chamber) and the weighing mechanism. The fact is that if the weighing mechanism is connected to the sample atmosphere it could be damaged or disturbed by the measuring process. Another limitation of those conventional gravimetric instruments is in the small size of the sample chamber and limited sample weight that some of those instrument can weigh, which reduce the field of applications since only small amount of powder, granules or films could fit the sample chamber.

Our project called for a gravimetric system which can meet our requirements, which includes long-term stability and high accuracy for testing of the high barrier materials; a large chamber to hold different shapes of sample (i.e. containers); various sorption conditions, such as generation of moisture and organic vapor, or a mixture of multiple organic vapors simultaneously. The gravimetric system used in this work was customized to meet our requirement. It has a big sample chamber, a large weighing range (up to 10 g), and the separation of sample chamber and weighing mechanism. Furthermore, this electrobalance can re-zero throughout the measuring process to reduce the drifting and noise. Thus it is necessary to address each part of this gravimetric system in detail.

The objectives of this work were to quantify the noise level of the new SGA-100R gravimetric analyzer and to develop a methodology to evaluate the sorption of organic and/or moisture vapor by continuously gravimetric method using SGA-100R. For this initial study, the sorption of benzaldehyde vapor on polypropylene resin, sheet and thermoformed sheet into a polyhedron shape have been considered.

3.2. Experimental

3.2.1 Gravimetric Instrument

Sorption studies were conducted on a SGA-100R gravimetric analyzer (VTI Corporation, Scientific Instruments, Hialeah, Florida) by the continuous flow method (Hernandez, 1986b; Nielsent, 1994). The gravimetric instrument includes three separate zones: Zone one is the weighing mechanism (microbalance head), zone two is the sample chamber, and zone three includes the vapor generators. Each zone includes its own

temperature control system in order to maintain instrument stability and overcome any environmental changes. The flow schematic of the gravimetric system is shown in Figure 3.1.

Zone one – Rubotherm electrobalance

The core portion of this gravimetric system, the Rubotherm electromagnetic suspension microbalance, is located in zone one. Instead of hanging directly at the balance, the sample to be investigated is linked to a suspension magnet, which consists of a permanent magnet, a sensor core, and a device for decoupling the measuring sample. The electromagnet, which is located at the bottom of the balance head in zone 1, maintains a freely suspended state of the suspension magnet *via* an electronic control unit. Using this magnetic suspension coupling the measuring force is transmitted contactlessly from the measuring chamber to the microbalance, which is located outside the chamber under ambient atmospheric conditions.

The measuring load can be automatically decoupled, as shown in Figure 3.1 (bottom). The load decoupling is carried out by lowering the suspension magnet in a controlled way to a zero point position. This position where only the weight of the suspension magnet is transmitted to the balance, corresponds to an empty balance pan in a normal weighing procedure. Now the balance can be tared and calibrated even when recording measurements under process conditions. This feature increases the measuring accuracy, particularly in the case of long-term measurements.



Figure 3.1. Schematic of gas flow in the Rubotherm SGA-100R gravimetric analyzer (top) and the coupling/decoupling action between the electromagnet and suspension magnet under different operation conditions (bottom).

Zone two - Sample chamber

The chamber has been designed in the dimension of 7.5cm×7.5cm×14cm (L×W×H), which is larger than conventional gravimetric instruments. It could weigh samples up to 10g with 1µg resolution. The temperature of the sample chamber and balance neck, which is located between balance head (Zone 1) and chamber (Zone 2), are controlled and maintained by two separated bathes filled with thermostated fluid to keep the temperature constant. The temperature of the entire volumes of the chamber could be set within a range between 25°C to 325 °C. The specific temperature setting is achieved by means of double-walled thermostating tubes, which completely surround the measuring cell and suspension balance, through the tubes a thermostated liquid is circulating. In this project, water was used as the thermostated liquid to control the temperature in the system.

A polymeric sample is placed either in the stainless steel sample basket or directly hung on the weighing hook. A constant concentration of sorbate vapor was generated in Zone three and was carried to the sample chamber. In order to maintain an even vapor generation the excess of vapor was discharged through a vent placed on the top of the chamber.

Zone three - Vapor generators

A parallel vaporizers / mass flow controllers and chilled mirror dew point analyzer (DPA) are located at the bottom of the instrument in a thermally independent enclosure. Organic vapor is generated by a vaporizer and mixed with dry nitrogen through the dry mass flow controllers and bypasses the DPA to enter the sample chamber. If moisture is used as a sorbate, then the mixture of nitrogen and moisture would enter the DPA before entering the chamber in order to verify the relative humidity (RH).

The organic vapor concentration generated by the vapor generator is controlled by adjusting the ingredients of mixed gas flow. With respect to the flow on the evaporators, the flow will change along with the temperature changes in the sample or in the evaporators. The sample temperature, which is controlled by the constant temperature bath, changes in the sorption test, typically less than ± 0.1 °C. Small changes like this scale are within the control specifics. The vapor activity is controlled within 0.00025 P/P_{o} (for organic this is the equivalent of $\pm 0.025\%$ vapor activity). Any changes greater than this, the system will adjust the flow automatically. The value of the activity of the solvent is measured by taking the sample temperature and the evaporator temperature. From the sample temperature, P_0 is determined by using the vapor pressure equation (Wagner Equation) (Golding, 1992). From the evaporator temperature, the vapor pressure of the solvent P is determined. Then the activity is calculated by dividing P by P_{o} . During this process, the only assumption was made by the manufacturer in the determination of activity of the solvent is that the evaporator is close to 100 % efficiency.

Important notes

For the best testing results the temperature setting for balance neck (Zone 1) and vapor

generators (Zone 3) should be 5-10 °C higher than that of the sample chamber (Zone 2). The purpose of this temperature setting is to help the vapor generation and to avoid the condensation of vapor/moisture on the balance neck or any inner parts in the channel above the sample chamber.

For those sorption tests involve any easily oxidized volatile compounds, such as benzaldehyde, the vent should be always opened to release any excess gases during the test and to avoid the condensation of the oxidized products.

The input and output of the instrument are controlled by a computer. The output of the sorption data could be various, including the sample weight / weight % change as a function of time, vapor activity, or sample temperature. The in-situ balance drifting can also be generated by plotting the zero-point shifting values as a function of time.

3.2.2 Materials

Organic sorbate. Benzaldehyde, purified by redistillation, \geq 99.5%, was obtained from Sigma-Aldrich Inc. (St. Louis, MO) and used as sorbate / permeant in this study.

Polymer. Polypropylene (PP) resin pellets were used as the starting material in this study. PP resin was obtained from ExxonMobil Chemical Company (Houston, Texas). The physical properties of PP resin are shown in Table 3.1.

Tg	-9.5 °C ª
Tm	164.9 °C ^a
Crystallinity	39.4 % ^a
Density	0.900 g/cm ^{3 b}
M _n	60,000 g/mol ^b
Mw	250,000 g/mol b
M _w /M _n	4.2 ^b
Total amount of additives	< 0.3 wt.% ^b

Table 3.1. Physical properties of PP resin

^a The information was obtained by differential scanning calorimetery (DSC Q100; TA Instruments, New Castle, DE)

^b The information was obtained from ExxonMobil Chemical Company (Houston, Texas)

Polypropylene sheet was produced by extrusion and casting from PP resin by Killion KLB100 extruder (Killion Extruder Inc., Cedar Grove, NJ). The PP sheet was formed in the thickness about 0.46 mm (~ 18 mil) and width of 15 cm (~ 6 in).

The polypropylene containers were thermoformed by sheet on a Hydro-Trim 1620 thermoformer (Hydro-Trim Corp., West Nyak, NY) using a male mold. The produced polyhedron container, as showed in Figure 3.2, has a surface area of 36.3 cm².



Figure 3.2. Polyhedron container thermoformed by male mold.
3.2.3 Quantification of Equipment Variability and Noise

There are several types of noise encountered in instrumental measurements. The first is white noise, which is due to the random motions of charge carriers such as electrons, the random motion results in voltage fluctuations. White noise includes thermal noise and shot noise. Drift is the second major type of instrumental noise. It is inversely proportional to the frequency of the signal being measured and is most significant for low frequencies. The third type of instrumental noise is that due to the surroundings of the instrument, such as power lines to the instrument or building vibrations (Robinson, 2005). The quantification of equipment variability and noise is necessary. They were measured right after the instrument setup to quantify the balance variability under different testing conditions.

To quantify the equipment variability under nitrogen flow, air (no vapor or nitrogen flow) and organic vapor flow, a piece of standard stainless steel in the weight of 100 mg was adopted due to the fact that the stainless steel won't absorb anything in the dry condition at room temperature. Initially the standard stainless steel weight was put in the metal sample holder (basket) while a stream of dry N₂ at 440 ml/min is constantly supplied to the sample chamber at 25 °C. The weight change was continuously recorded. In the next trial the standard weight/basket were suspended in air (without any flow of vapor or nitrogen), the weight change was also recorded. Finally, the standard metal weight/basket were suspended in the benzaldehyde vapor at testing concentrations. The weight change % for the standard weight/basket suspended under the different conditions was recorded over 4000 minutes.

3.2.4 Sorption test of benzaldehyde in PP (resin, sheet and polyhedron shaped sheet)

Once the gravimetric instrument had been calibrated, the sorption of benzaldehyde by different sample of PP were carried out. Prior to the sorption tests, the PP sample was dried by a vacuum oven (30 mmHg, 40 °C) for 10 hours. The pre-dried sample was placed in the sample chamber (Zone 2). The resin sample was placed in the basket, the sheet and the polyhedron shaped sheet were suspended directly on the hook.

Each sample was subjected to a sorption procedure including: (1) an initial drying period, where nitrogen was purged through the chamber for 2 hours at 25°C to ensure that the sample was completely dried and also to condition the sample and chamber; (2) exposing the sample to a specific benzaldehyde vapor activity; and (3) continuously monitoring and recording the weight change of the polymer sample in sorption until either equilibrium was reach or 10,000 minutes had passed. Five vapor activities (0.1, 0.3, 0.5, 0.7 and 0.9) were tested individually in the sorption study.

For the measurement of sorption curves, the actual sorption results needed to be compensated from the drifting of the balance at testing temperature. The balance was calibrated before each measurement and was tared every 10 minutes during the measurements. These procedures were done to correct for buoyancy on the suspension magnet and any inner parts that were lifted together with the sample in the magnetic coupling.

3.3. Results and Discussion

3.3.1 Evaluation of the Instrument Noise

The weight change % vs. time for the standard weight/basket suspended under the above mentioned three conditions are shown in Figure 3.3. The detailed analyses of the instrument noise and drifting are shown in Figure 3.4. The graphs located in the left column of Figure 3.4 are the weight change of the sample under the three conditions. The method of least squares for regression was adopted to study the instrument noise (Robinson, 2005). The graphs located at the right column in Figure 3.4 are the residual noise vs. time under the three conditions. The assumptions required for hypothesis testing in regression analysis is the residual noise $e_i \sim \text{NIID}(0, \sigma^2)$, e is normal distributed, the variance of e is constant across different values of x (time) and the value of one e_i should not depend on that of another e_i . The linear regression model for the experimental observation can be written as:

$$\mu_{y/x} = \beta_0 + \beta_1 x + e_i \tag{1}$$

where β_0 is the y intercept, and β_1 is slope of the regression line. The statistical analysis for all the three experiments is summarized in Table 3.2.



Figure 3.3. Quantification of equipment variability and noise: standard weight (100mg) was placed in metal basket in air, nitrogen flow and benzaldehyde flow at vapor activity of 0.1.

Table 3.2 Regression analysis of the instrumental noise and drifting

		AN	IOVA	X variable (β_1)		Amplitude
	Regression line	MSE	Significant	t-statistic	95% CI	of noise
			F		on β_1	(3s)
Metal in	<i>y</i> =	5.1*10 ⁻⁰⁵	0.0538	1.9310	[-7*10 ⁻⁹ ,	0.0214%
N ₂	$4*10^{-7}x-0.0068$				8*10 ⁻⁷]	
Metal in	<i>y</i> =	2.6*10 ⁻⁰⁵	0.9106	-0.1123	[-3.2*10 ⁻⁷ ,	0.0153%
air	2*10 ⁻⁸ x-0.015				2.8*10 ⁻⁷]	
Metal in	<i>y</i> =	1.7*10 ⁻⁰⁵	2.8*10 ⁻¹⁶⁹	48.2389	[8.2*10 ⁻⁶ ,	0.0124 %
VA0.1	$9*10^{-6}x-0.0054$				8.9*10 ⁻⁶]	
Metal in	y =	3.0*10 ⁻⁰³	1.05*10 ⁻³²	12.9455	[2.2*10 ⁻⁵ ,	0.165%
VA0.9	3*10 ⁻⁵ x+0.3218				3.1*10 ⁻⁵]	



Figure 3.4. Quantification of noise in Rubotherm SGA-100 gravimetric analyzer. The black dots are experimental data, the gray line is the least squares regression line. Left column shows weight change % vs. time for the standard weight. Right column shows the residual output corresponding to the experimental data in the left.

For the first experiment, in which the weight change of standard weight was monitored under nitrogen flow, the significance F of 0.05383 shows the linear regression line fits data statistically based on the Type I error α of 0.05. The residual variance (MSE) is 5.0852*10⁻⁰⁵, thus the least squares regression line with the equation of $y = 4*10^{-7}x -$ 0.0068. The P-value for X variable is 0.0538 indicates we fail to reject the hypothesis H₀: $\beta_1 = 0$, thus the slope of the linear regression line is 0, meaning no drift.

The residual output is shown in the right column of Figure 3.4. Based on the empirical

rule, $\mu_{y/x} \pm 3s$ contains 99.7 % of the distribution. Thus the amplitude of the noise is 0.0214 % for the metal in N₂ based on the Type I error of 0.003.

For the data obtained form the noise evaluation when the standard weight was exposed in a benzaldehyde vapor at a vapor activity of 0.1 and in air, the equivalent procedure as described above was carried out.

Based on the statistic data in Table 3.2, we concluded that under the Type I error of 0.05, the linear regression line fits data obtained when the standard weight is suspended under nitrogen flow or air, but does not fits well when the standard weight is suspended under benzaldehyde at vapor activity of 0.1.

There is no drifting observed for standard weight suspended under nitrogen flow or air, but the drifting is observed when standard weight is suspended in benzaldehyde at vapor activity of 0.1. The slope in the last case is $9*10^{-6}$ with the 95% confidence interval of $[8.2*10^{-6}, 8.9*10^{-6}]$. The noise amplitudes of these three conditions are 0.0214%, 0.0153% and 0.0124%, respectively.

The instrument noise was also investigated at the five vapor activities (0.1, 0.3, 0.5, 0.7 and 0.9) under which the sorption studies were carried out. The slopes of drifting at each condition were $0.9*10^{-5}$, $1.5*10^{-5}$, $2.1*10^{-5}$, $2.7*10^{-5}$ and $3*10^{-5}$, respectively.

3.3.2 Equilibrium Criterion Determination

Equilibrium is a state in which the chemical potential of the compound is the same in both phases (fluid phase and polymer phase). In a sorption study by the gravimetric method, the equilibrium is controlled and determined by an equilibrium criterion. The equilibrium criterion was set as the weight change of less than 0.0001 % in 20 mins. In this setting, if the weight change of the sorption system is less than 0.0001% in 20 mins, the equilibrium will be considered to have been reached.

The experimental results showed that the sorption of benzaldehyde in PP resin behaved differently at different vapor pressures. The sorption at high vapor activities (0.7 and 0.9) was similar and much more complicated than the sorption at relatively low vapor activities (0.1-0.5).



Figure 3.5. Sorption curve for benzaldehyde vapor in PP resin at vapor activity of 0.5 at 25 °C. The black dots are the experimental data; the gray line is the polynomial curve fitting of the sorption data in the post Fickian region.

Figure 3.5 shows the sorption curve of resin at a vapor activity of 0.5, which represents the sorption of PP resin at low vapor activities (0.1-0.5). The curve exhibited a linear initial slope and then it bent toward the x axis (zero slope) to a protracted behavior starting from 1000 min towards the end of the sorption (10,000 min). The gray line is the regression fitting of the sorption data in the 1000-10000 min domain. The slope of the regression line ($5*10^{-6}$) is less than the instrument drift at a vapor activity of 0.5 (2.1*10⁻⁵), which has been analyzed in section 3.3.1. Thus it indicated that the protracted sorption within the 800-10000 min domain in Figure 3.5 was caused by the balance drifting but not by sorbate uptake. The equilibrium was reached under the test condition. The wavy sorption character exhibited along the gray line with the amplitude of 0.009% was caused by the instrument noise.



Figure 3.6. Sorption curve for benzaldehyde vapor in PP resin at vapor activity of 0.7 at 25 °C. The black dots are the experimental data; the gray lines are the polynomial curve fitting of the sorption data in the post Fickian regions.

The sorption curve of PP resin at vapor activity of 0.7 is shown in Figure 3.6, which represents the sorption of PP resin at high vapor activities (0.7-0.9). The curve exhibited a linear initial slope and it bent to the first equilibrium mass uptake at 1300 min. This behavior is one key characteristic of sorption kinetics controlled by Fickian diffusion. However, after the initial Fickian region, the mass uptake exhibited a protracted, wavy behavior towards the end of the sorption. The gray lines with slope of $3*10^{-5}$ and $6*10^{-6}$ are the regression fitting of the sorption data in the post Fickian regions, namely second region and third region, respectively. The second sorption region showed the continuous sorbate uptake by the resin after the initial Fickian region, since the slope $(3*10^{-5})$ is larger than the instrument drift at a vapor activity of 0.7 (2.7*10⁻⁵). The third sorption region has a slope $(6^{*}10^{-6})$ smaller than the instrument drift, thus it was due to the balance drifting but not to sorbate uptake. Finally, the sorption reached the equilibrium in the third region.

In this study, the sorption took place in the rubbery PP at 25 °C, which is well above the glass transition temperature (T_g) of PP (T_g determined by DSC is -6.4 °C). It was expected that sorption of benzaldehyde in rubbery polymer exhibits only Fickian kinetics. As mentioned above, Fickian sorption kinetics was observed at low vapor activities (0.1-0.5). However, sorption at high vapor activities (0.7 and 0.9) resulted in more complex sorption behavior. Such phenomenon is so called "two-stage kinetics" and is often observed for organic vapor sorption in glassy polymers (McDowell, 1999; Crank, 1975). Rossi and Mazich (1993) showed that non-Fickian sorption curves can be obtained for solvent diffusion in rubbery polymers under certain conditions, such as when a spherical geometry was used and the swelling of the polymer and the existence of a moving boundary were properly taken into account. The mass transfer problem could be solved numerically using Fick's law and the standard boundary conditions and obtained apparently anomalous sorption curves. The geometry of the specimen was found to play a special role in the sorption and was essential in determining the shape of the sorption curves. The influence of geometry and moving boundaries on sorption of solvent in rubbery polymers was mentioned and described by Vrentas (1998).

3.3.3 Sorption of Benzaldehyde in PP

The sorption of benzaldehyde by PP resin was studied by continuously recording the weight gain of the polymer sample when exposed to certain concentrations of benzaldehyde vapor until equilibrium was reached. The sorption curves for the five vapor activities are shown in Figure 3.7. The two-stage sorption was observed in the sorption curves of the resin at high vapor activities (0.7 and 0.9). The higher the vapor activity, the more the weight uptake by the PP resins.

The sorption curves for benzaldehyde in PP resin, sheet, and polyhedron container at a vapor activity of 0.9 at 25 °C are shown in Figure 3.8. The two-stage sorption is observed in the sorption curves of PP resin, and PP polyhedron container exhibited a Fickian sorption kinetics. Besides, the sorbate uptake in PP resin, sheet and container are significantly different based on the Type I error of 0.05.



Figure 3.7. Sorption curves for benzaldehyde vapor in PP resin at 25 °C. From top to bottom, the vapor activities are 0.9, 0.7, 0.5, 0.3, and 0.1, respectively.



Figure 3.8. Sorption curves for benzaldehyde vapor in PP resin, sheet, and polyhedron container at vapor activity 0.9 at 25 °C.

We believe that the sorption difference among these PP forms is caused by the polymer processing. During the procedure we extruded and cast the sheet from resin, and thermoformed the sheet to container, the material was exposed to thermal processes, the polymer morphology was changed causing changing in sorption characteristics. Thus the morphology, the surface to bulk ratio and material orientation were changed throughout the processing, all these factors affect the sorption behavior of benzaldehyde in the different forms of PP.

3.4. Conclusion

A gravimetric method was developed to evaluate the sorption of benzaldehyde by PP resin *via* a SGA100R gravimetric system including a Rubotherm magnetic suspension electrobalance. The balance drifting due to the buoyancy was corrected during the test. The instrument variability and noise were studied before the sorption study. The drift was observed at the test conditions varied from $2*10^{-8}$ to $3*10^{-5}$. The Noise was observed and the amplitude was in the range of 0.0124% to 0.165%. The instrument stability still need to be improved.

The sorption of benzaldehyde in PP resin at different vapor activities was studied and the sorption behavior among the different PP forms (resin, sheet and polyhedron container) was compared. It was found that the sorption of benzaldehyde in the PP polyhedron container was almost twice that of the sorption in PP sheet, and the sorption in sheet was almost four times the sorption of the resin at a vapor activity of 0.9.

This study showed that the SGA-100R with Rubotherm magnetic suspension microbalance is capable of measuring sorption continuously, and the results are relatively stable and highly accurate due to the separation of the balance magnetic and the measuring cell. The three vapor generators in the balance offer the possibility to study the sorption and migration under pure organic vapor/moisture conditions or more mixed vapor conditions. The large chamber makes it possible to study the sorption by large polymer objects, such as a containers. All these advantages make the SGA-100R an efficient and precise tool in exploring the mass transfer properties of polymer materials.

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CHAPTER 4

Impact of Polymer Processing on Sorption of Benzaldehyde Vapor in

Semicrystalline Polypropylene

This chapter is preparing for the submission to the journal of Macromolecules.

Impact of Polymer Processing on Sorption of Benzaldehyde Vapor in Semicrystalline Polypropylene

Abstract

Organic vapor sorption properties of different polypropylene (PP) forms (resin, sheet, thermoformed sheet and atatic PP) at 25 °C are reported. The sorption of benzaldehyde at five vapor activities was studied by using continuously gravimetric method via a SGA100R gravimetric analyzer including Rubotherm magnetic suspension electrobalance. The sorption of benzaldehyde vapor in PP exhibits different behaviors among resin, sheet and polyhedron thermoformed sheet. The two-stage sorption was observed in resin at high vapor activities (0.7, 0.9), but not in sheet and thermoformed PP sheet. The solubility coefficient was calculated based on equilibrium sorption data. The diffusion coefficient was calculated only in the Fickian diffusion region. The experimental results demonstrated that polymer processing has great impact on the sorption behavior, especially at high vapor activities. The processing changed the polymer morphology and surface structure thus changed the sorption behavior of polymer.

Keywords: Sorption, benzaldehyde, polypropylene, gravimetric method, processing, morphology

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4.1 Introduction

The use of polymers as food and pharmaceutical packaging materials has experienced rapid and continuous growth in recent years. Along with the increasing use of new high barrier and biodegradable polymers in packaging application, there is a need to access mass transfer phenomena of multiple compounds as applied to polymer and packaging science.

Mass transfer process between the polymer and the product and or environment can be described as a multi-step event, including collision of the penetrant molecule with the polymer followed by sorption in the polymer, migration through the polymer matrix by diffusion, and finally, desorption of the permeant from the polymer (Klopffer, 2001). Mass transfer properties of polymer, especially sorption and diffusion properties are determined by the chemical structure of the chain, the polymer morphology, surface area and processing. For a selected pair of sorbate and polymer at certain environmental conditions, the sorption is mainly controlled by the polymer morphology, such as crystallinity, free volume, and processing history.

Crystallinity. As postulated by Michaels *et al.* (Michaels, 1961a,b; Michaels, 1959), the concept that the sorption and diffusion takes place exclusively in the amorphous regions has been widely accepted. The crystalline zones act as excluded volumes for the sorption process and are impermeable barriers for the diffusion process. The dispersed crystalline phase presents a resistance to the permeant passage. More exactly, Klopffer

(2001) indicated that these crystalline zones have two effects on the gases diffusion: on one hand, they increase the effective path length of diffusion; and on the other hand, they seem to reduce the polymer chain mobility in the amorphous phase because the chain ends are trapped in the neighboring crystalline lamellae, and then lead to higher activation energy of diffusion. Michaels *et al* (1961 a,b; 1959) thus introduced a "tortuosity factor" τ and a "chain immobilization factor" β to account for these effects.

Free volume. In the case of amorphous or semicrystalline polymers, the solubility and diffusion coefficients (S) and (D) can be related to the free volume ($V_{\rm f}$), which is defined as a space which is not occupied by the macromolecules and its value is equal to the difference between the specific and the occupied volumes of the polymeric system (Danch, 2003). According to Fujita's free volume theory (1960), it's possible to explain the dependence of D with parameters such as the concentration, the penetrant shape and size, the temperature and the glass transition temperature of the polymer.

Processing. Forming process of a polymer, such as extrusion, blow molding, injection blow molding and thermoforming, by which film / sheet are converted into containers or automotive parts, etc, changes the polymer structure and morphology. The conversion of polymer resin, film/sheets into shaped objects is carried out under high pressure and temperature, these conditions induce localized effects and stresses in the final thermoformed polymer causing changes in the morphology and consequently variations in the barrier property among unformed resin, extruded sheet and thermoformed or shape objects, such as containers (Jasse, 1994). Due to the difficulties on the testing of mass

transfer of organics in polymeric shaped objects, much of the current permeability data of organic compounds has only been obtained on flat films or sheets, and these values were then used to calculate the barrier properties of shaped objects (Hernandez, 1992; Nir, 1996). Obviously large error could be generated in the prediction of the container barrier properties by using the permeability data generated from film or sheet.

Vapor activity (VA). In general, permeant concentration has no effect on sorption at low vapor activities (VA = p/p_s) for organic compounds, all in the range of Henry's Law. While strong effect can be found for organic compounds at high value of activity (Vittoria, 1993).

Interaction of polymer and organic solvent. Inherent in studying polymer-solvent applications is the necessity of exploring the complex changes in polymer properties as the polymer undergoes vapor sorption. Upon vapor sorption not only does a polymer gain mass, but structural changes within the polymer may occur, such as relaxation effects of the polymer side chains, free volume variations, glass transition temperature lowering and an increase in viscoelastic behavior (Buchold, 1999). Sorption of gases and vapors has been extensively studied in polypropylene (Sato, 2001; Palamara, 2005; Ochiai, 1971). However, the sorption behavior can be complicated by concentration and time dependence of diffusion coefficients, and also the fact that polymer sorption and swelling are specific for each polymer and dependent on the processing conditions. Meanwhile, to the best knowledge of the authors, no data on the comparison of sorption of benzaldehyde vapor in polypropylene sheet and formed sheet have been reported so far, and neither has the effect of polymer processing been addressed on sorption of organics in polymers. The aim of this work is to fill in this gap.

The objective of this work is to demonstrate the impact of processing of PP from resin to sheet and formed polyhedron shaped sheet on the sorption of benzaldehyde vapor.

4.2 EXPERIMENTAL AND METHOD

4.2.1 Materials

Benzaldehyde, purified by redistillation, \geq 99.5%, was obtained from Sigma-Aldrich Inc. (St. Louis, MO) and used as sorbate / permeant in this study.

Atatic polypropylene (PP), a totally amorphous waxy solid with specific gravity 0.85 g/cm^3 and M_w of 12,000 g/mol, was obtained from Scientific Polymer products, Inc (Ontario, NY).

PP resin pellets were obtained from ExxonMobil chemical company (Baytwon, TX).

4.2.2 Polymer Processing

PP sheets in the thickness of 0.46 mm (18 mil) and width of 15 cm (~ 6 in) were formed by extrusion and casting from PP resin by Killion KLB100 extruder (Killion Extruder Inc., Cedar Grove, NJ). PP polyhedron container (thermoformed sheet) with surface area (36.3 cm²) was designed to represent those containers that have several corners and edges. The polyhedron polypropylene containers were thermoformed from sheet by using a Hydro-Trim 1620 thermoformer (Hydro-Trim Corp., West Nyak, NY) through male mold. The designed male mode and thermoformed polyhedron container are shown in Figure 4.1.



Figure 4.1. Male mold (left) and thermoformed polyhedron shape (right).

4.2.3 Gravimetric Method

Gravimetric method is very suitable for the study of sorption and diffusion. The advantages of gravimetric method are not only the simplicity in the manipulation of the polymer sample, but also the possibility of continuously recording the weight gain by the test specimen as a function of time. Furthermore, the gravimetric method permits an accurate and direct measurement of the sorbate uptake at both transient and steady states.

Sorption studies were conducted on a SGA-100R gravimetric analyzer (VTI Corporation, Scientific Instruments, Hialeah, Florida) including a Rubotherm magnetic suspension electrobalance by the continuous flow method (Hernandez, 1986a; Nielsent, 1994). The core portion of this system is the electromagnetic suspension microbalance (Krüger, 2005; Qin, 2006), that measures the weight change of the sample. The electromagnetic suspension microbalance makes it possible to weigh samples with a contactless magnetic suspension coupling under nearly all environments with a balance located under ambient conditions. This SGA100R has been designed to meet our requirement with a chamber in the dimension of 7.5cm×7.5cm×14cm (L×W×H), which is large enough to hold a thermoformed sheet / plastic container sample; also, the vapor activity (VA) / relative humidity (RH) is generated and constantly maintained by vaporizer / humidifier. Also there are three vapor generators in this system, which allow the generation of mixed gas atmosphere within the sample chamber; the data is continuously recorded by setting at certain time interval. Besides, the balance is designed to have long-term stability due to the separation of the measuring cell and the weighing system. The automatic decoupling of the measuring load / rezero throughout the testing process increases the measuring accuracy particularly in the long term measurements. Further description of the electrobalance, including instrument details, instrument noise and drifting analyses under different conditions can be found elsewhere (Qin, 2006).

4.2.4 Experimental Procedure

The sorption data was compensated from the drifting of the balance at 25 °C. The balance was calibrated before each experiment and during the measurements and the balance drift was corrected every 10 minutes. These were done to correct for buoyancy

on the suspension magnet and any inner parts of the magnetic coupling which were lifted together with the sample.

Prior to the sorption tests, the polymer sample was dried in a vacuum oven at 40 °C for 10 hours. It was then purged with N_2 for 2 hours in the balance chamber. The sorption tests were conducted at five benzaldehyde vapor activities (0.1, 0.3, 0.5, 0.7 and 0.9). The weight gain of the polymer sample was continuously monitored and recorded at 25°C and 0% relative humidity. The balance equilibrium criterion was the weight change below 0.0001 % in 20 mins. Experiments were continued until the sorption equilibrium was reached or 10,000 minutes had been passed.

4.3 Results and Discussion

4.3.1. Impact of Surface Area and Bulk Properties on the Sorption of Benzaldehyde in PP Resin

Sorption of organics in polymer films had been studied thoroughly. However, the sorption behavior in polymer resin pellets has not yet been completely elucidated. The sorption took place in the rubbery PP resin pellets at 25 °C, which is well above the glass transition temperature of PP (T_g of -6.4 °C). Unlike what was expected for the sorption of benzaldehyde on rubbery polymer, the PP resin did not just exhibit a simple Fickian kinetics. In our previous work (Qin, 2006), as showed in Figure 4.2, it has been found that at high vapor activities (0.7 and 0.9), the sorption curve exhibited a linear initial slope

and it bent to the first equilibrium mass uptake at 1300 mins. At extended time, the mass uptake exhibited a protracted, non-Fickian behavior. Such phenomenon is so called two-stage kinetics and is often observed for organic vapor sorption in glassy polymers (McDowell, 1999; Rossi, 1993). However, it has been shown by Rossi and Mazich (1993) that non-Fickian sorption curves can be obtained for solvent diffusion in rubbery polymers under certain conditions when a spherical geometry was used and the swelling of the polymer and the existence of a moving boundary were properly taken into account.



Figure 4.2. Sorption curve for benzaldehyde vapor in PP resin at vapor activity of 0.7 at 25 °C. The black dots are the experimental data, the arrow shows the first Fickan region.

Sorption of benzaldehyde vapor in isostatic PP resin pellets was first assessed by studying the sorption in relatively small amount of resin pellets (0.15g), large amount of

resin pellets (2.0 g), resin slices (cut from resin pellet), and in atatic PP (totally amorphous). The result is shown in Figure 4.3.





The sorption curves a) and b) are the sorption of benzaldehyde in PP resin pellets but in different starting dry weight. The pellets in these tests came from the same batch, they had an average diameter of 0.4 cm. Based on the sorption result of curve a and b, we found that the uptake of benzaldehyde vapor in a different amount of polymer resin had a similar result (weight change is 0.130 % for curve a and 0.131 % for curve b). Thus we conclude that the sorption result does not depend on the polymer starting dry weight.

The PP resin pellets were further processed for the purpose of testing the surface effect on the sorption. Each resin pellet was cut into 8 slices. Sorption curve c) in Figure 4.3 represents the sorption in PP resin slices in the similar weight of that in resin pellets (curve a). The result showed that the sorption of benzaldehyde in whole resin pellets (curve a) and in resin slices (curve c) are 0.13 % and 0.50 %, individually. The extra weight gain of resin slices was benefited from the larger surface area compared with whole resin pellets. This study clearly demonstrated the surface area (surface morphology) does affect the sorption. It encouraged us to further explore the other morphology factors control the sorption behavior.

The atatic PP (100% amorphous) was thus studied in the sorption experiment. The sorption result of benzaldehyde in atatic PP (curve d) was compared with that in resin pellets (curve a) in Figure 4.3. Very clear sorption difference between atatic PP (1.90 %) and isostatic PP resin pellets (0.13 %) were observed in the tests. PP resin pellets are semi-crystalline material with crystallinity of 39.4 % and density of 0.90 g/cm³. The atatic PP has 0 % of crystalline and density of 0.85 g/cm³. Since sorption and diffusion took place exclusively in the amorphous regions and the crystalline zones are impermeable barriers for the diffusion process, it is predictable that atatic PP absorbs more than that of semicrystalline resins, as the sorption result shown in Figure 4.3.

As a result, it was found that the surface area as well as morphology of the bulk of the polymer material had major impact on the sorption process.

4.3.2 Sorption of Benzaldehyde in Different PP shapes

Figure 4.4 shows the sorption of benzaldehyde by PP resin, sheet, thermoformed sheet and atatic PP studied by continuously recording the weight gain of polymer when exposed to benzaldehyde vapor at vapor activity of 0.3 at 25 °C. Based on the sorption curves in Figure 4.4, we found that the thermoformed sheet gained more weight (0.489 %) than PP sheet (0.271 %) and resin (0.077 %) at same vapor pressure. This demonstrates the fact that any processing, to which the resin was subject, caused an increase of the sorption of benzaldehyde.



Figure 4.4. Sorption curves for benzaldehyde vapor in PP with vapor activity of 0.3 at 25 °C. From bottom to top: sorption in a) resin pellets, b) sheet, c) thermoformed sheet and d) atatic PP.

Normally when polymer is processed, the internal stresses will be set up and the heat treatment during the processing imparts the molecular chains energy and mobility to rearrange themselves towards the conformational changes. The polymer morphology, including crystallinity, crystal size, the distance between the lamellas, free volume and surface contour will all be changed according to the processing conditions. As mentioned before that sorption behavior of polymer is closely related to the polymer morphology, thus the polymer processing, which causes morphology changes, should cause different sorption behavior for different thermoprocessed polymers. The processing effect on sorption is clearly demonstrated in Figure 4.4. Furthermore, the sorption of benzaldehyde in atatic PP was used as a reference to compare with that in other PP forms (resin, sheet and thermoformed sheet). The high sorption ability of atatic PP (0.989 %) supports the morphology effect in the organic sorption in polymer.

4.3.3 Impact of Vapor Activity of Benzaldehyde on the Sorption Behavior

The processing effect on the sorption of benzaldehyde in PP has been demonstrated in Fig.4.4 at vapor activity of 0.3. The similar processing effect was also observed in vapor activity of 0.5 and 0.9. The comparison is shown in Figure 4.5. It is found that for each PP form (resin, sheet, thermoformed sheet or atatic PP), the sorption capability increases as the organic vapor pressure increases. Besides, the higher the VA, the larger the sorption difference was observed among the different PP forms.



Figure 4.5. Sorption curves for benzaldehyde vapor in PP at 25 °C at vapor activity of 0.5 (left) and 0.9 (right). From bottom to top: PP resin, sheet, thermoformed sheet and atatic PP.

4.3.4. Benzaldehyde Sorption Isotherm

The gravimetric sorption experiments were used to study the sorption of benzaldehyde on PP resin at 25 °C till reaching equilibrium. The position and shape of specific isotherms were determined by the polymer-penetrant interaction parameter and the glass composition of the system. The sorption isotherm for benzaldehyde - rubbery PP resin at 25 °C is shown in Figure 4.6.



Figure 4.6. Sorption isotherm of benzaldehyde by PP resin at 25 °C. The isolated squares are experimental data; the dashed line is the trend line based on experimental data

The isotherm shape in Fig.6 is typical of that for isotherm of organic vapors in rubbery polymers. Thus, the Flory-Huggins equation (1) was used to describe the sorption behavior (Berens, 1989).

$$\ln(P/P_0) = \ln(V_1) + (1 - V_1) + \chi(1 - V_1)^2$$
(1)

where χ is the interaction parameter, V_1 is penetrant volume fraction. P and P_0 are actual and saturated vapor pressure at certain temperature, respectively. The percent weight gain, (%Wt. Gain), is related to the volume fractions of solvent and polymer, V_1 and V_2 , respectively, by

%*Wt.Gain* = 100
$$\cdot \frac{V_1 d_1}{V_2 d_2}$$
 (2)

where d_1 and d_2 are the solvent and polymer densities.

Interaction parameter χ from Hansen Solubility Parameters (HSP)

The Flory-Huggins interaction parameter χ , has been used for many years in connection with polymer solution behavior, with the χ_{12} parameter derived from the "New Flory Theory" being currently accepted for general use instead of the older χ . It would be desirable to relate the widely used HSP more directly to χ_{12} . This would allow estimates of χ_{12} for systems where the HSP are known, but χ_{12} is not (Hansen, 1999). Patterson and co-workers have shown that χ_{12} can be calculated (Biros, 1971).

$$A_{12} = [(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2]$$
(3)

and χ_{12} is estimated from: $\chi_{12} = \frac{VA_{12}}{RT}$ (4)

where δ_D , δ_P and δ_H are the Hansen Solubility Parameters representing the contributions from the dispersion interaction, polar interaction, and hydrogen bonding, respectively; and the subscript 1 and 2 are for solvent and polymer, respectively. V is molecular volume of solvent. R is the gas constant $(m^3 Pa)/(mol K)$. T is temperature in Kelvin. The Hansen Solubility Parameters for benzaldehyde and PP are shown in Table 4.1. The χ_{12} is calculated as 1.29 based on the equation (3) and (4) for benzaldehyde and polypropylene pair at 25 °C. Combined the χ value with the calculated solubility parameter of benzaldehyde PP group contribution method $\Delta \delta_{\rm T}$ = and by 93.7 $(\Delta \delta_T = [(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2]^{1/2}$ (Caner, 2004), we can characterize benzaldehyde as a weak swelling agent to PP.

	÷۲	, ,	
	$\delta_{ ext{D}}$	δρ	$\delta_{ m H}$
Benzaldehyde	19.4	7.4	5.3
Polypropylene	16.1	0	0

Table 4.1. Hansen Solubility Parameters Data for Benzaldehyde and Polypropylene at 25

The experimental equilibrium sorption data for benzaldehyde were compared with the Flory-Huggins equation with $\chi_{12} = 1.29$. It was found that sorption data could not fit well into the Flory-Huggins equation at vapor activity of 0.1 to 0.9 with this χ value. As far as the authors' knowledge, solubility in PP resin as a function of solvent activity for benzaldehyde has not been reported in the literature. Our result suggests that the Flory-Huggins equation, with interaction parameters determined from equilibrium sorption of the pure liquids, could not provide sufficient estimates of sorption isotherms for benzaldehyde vapor – PP resin system.

The Flory-Huggins theory is useful in considering the thermodynamics of dilute polymer solutions. The interaction parameter χ_{12} characterizes a polymer-solvent pair and has been used in connection with polymer solution behavior (flory, 1953), but it has some theoretical limitations (Barton, 1991). The interaction parameter χ_{12} is not a constant, and depends on polymer concentration and molecular weight as well as temperature. It is a composite term influenced by factors such as hydrogen bonding, and polymer characteristics. In our study, PP resin pellets were used in the sorption instead of films, which were generally used by sorption studies. The density and chain matrix of PP resin varied from the commercial PP films or the forms Hansen Solubility Parameters had been generated from. Besides, most of the sorption kinetics studied by Flory-Huggins equation have % Wt. Gain in the scale of above ten percent. While in this study, the maximum weight gain was only 0.31%, which is around 30 times less than the reported values for other solvent-polymer systems. The combination of factors described above might cause the deviation of the experimental data away from theoretical Flory-Huggins equation. Further theoretical models need to be explored and adjusted.

4.3.5 Equilibrium Benzaldehyde Sorption and Sorption Kinetics Measurements

These equilibrium organic uptakes in sorption experiments were used to calculate the solubility coefficient (S). S is an equilibrium partition coefficient for distribution of the penetrant between polymer and vapor phase. It is a measure of the mass of permeant molecules sorbed by a unit of polymer mass per unit of partial pressure, and it is defined according to equation (5) (Nielsent, 1994; Barr, 2000):

$$S = \frac{M_{\infty}}{v \cdot p} \tag{5}$$

where M_{∞} is the total amount (mass) of vapor absorbed by the polymer at equilibrium for a given temperature, v is the volume of the polymer sample, and p is the penetrant driving force in unit of pressure. S, in the unit of kg/m³Pa, was calculated by multiplying the weight gain (kg of sorbate per kg of polymer) by polymer density and divided by vapor pressure. The calculated solubility coefficients for the sorption of benzaldehyde by PP at 25 °C are shown in Table 4.2. The broken line means the solubility coefficients are not available since the equilibrium was not reached in the sorption test. For resin, the equilibrium was reached at all vapor activities except at vapor activity of 0.1, the *S* data is not available due to the weight gain % is close to the instrument noise (Qin, 2006).

As we studied the sorption of benzaldehyde in various PP forms, we found that sorption in resin at high vapor activities exhibited two-stage sorption at 25 °C, the first equilibrium mass uptake showed the sorption kinetics was controlled by Fickian diffusion. Thus it is possible to deduct a diffusion coefficient (*D*) in the Fickian region for each curve with vapor activity from 0.1 to 0.9 (Krüger, 2005). For sorption in PP sheet, one-stage sorption was observed, *D* could be calculated when the equilibrium was reached. For this purpose each sorption curve is plotted as M_t/M_{∞} vs. $t^{1/2}$ as the demonstration of the VA=0.5 step in Figure 4.7.



Figure 4.7. Sorption curve for benzaldehyde vapor in PP resin at 25 °C with vapor activities of 0.5. The inner small figure is the plot of M_t / M_∞ vs. $t^{1/2}$ in the initial Fickian region

The benzaldehyde sorption kinetics for PP resin could be measured by the method applied for polymer sphere or powder. The ratio of the amount of vapor absorbed at any time (t) over the equilibrium sorption level at infinite time (M_t / M_{∞}) for polymer samples of spherical geometry and of diameter (d) is given by the expression (Hernandez, 1986a):

$$\frac{M_{t}}{M_{\infty}} = 1 - \frac{6}{\pi^{2}} \left[\exp(\frac{-4D\pi^{2}t}{d^{2}}) + \frac{1}{4} \exp(\frac{-16D\pi^{2}t}{d^{2}}) \right]$$
(6)

The diffusion coefficient (D) is readily obtained from the above equation by setting M_t / M_{∞} equal to 0.5 and solving to give the expression:

$$D = 7.45 \bullet 10^{-3} \bullet \frac{d^2}{t_{0.5}} \tag{7}$$

Similarly, the sorption kinetics for PP sheet can be obtained by equation (8) and (9) (Hernandez, 1986a; Nielsent, 1994):

$$\frac{M_{l}}{M_{\infty}} = 1 - \frac{8}{\pi^{2}} \left[\exp(\frac{-D\pi^{2}t}{l^{2}}) + \frac{1}{9} \exp(\frac{-9D\pi^{2}t}{l^{2}}) \right]$$
(8)

l is the thickness of the sheet. The sorption diffusion coefficient (D_s) can be calculated from the above equation by setting M_t / M_∞ equal to 0.5 and solving to give D_s :

$$D_s = \frac{0.049l^2}{t_{0.5}} \tag{9}$$

The diffusion coefficient for the initial Fickian sorption stage for sorption of benzaldehy by PP at different vapor activities were calculated and are shown in Table 4.3. The broken line means the diffusion coefficients are not available since the equilibrium was not reached at the end of the sorption test. In general, the diffusion coefficients in resin in the Fickian region are found much larger than that in sheet under testing vapor pressures.

Vapor activity	Resin		Sheet		Thermoformed sheet (Polyhedron container)	
	% Wt. Gain	S Kg∕(m ³ ·Pa)	% Wt. Gain	S Kg∕(m ³ ·Pa)	% Wt. Gain	S Kg/(m ³ ·Pa)
[pa/pa]	[%		[%		[%	
	g _b /g _{pp}]		g _b /g _{pp}]		g _b /g _{pp}]	
0.1			0.053	0.030	0.189	
0.3	0.075	0.014	0.150	0.028	0.489	
0.5	0.085	0.010	0.798		0.899	
0.7	0.275	0.023	1.087		1.140	
0.9	0.440	0.028	1.735		3.135	0.191

Table 4.2. % Wt. Gain and calculated solubility coefficient (S) for benzaldehyde- PP at

25 °C

Table 4.3. Calculated Fickian diffusion coefficient (D) for benzaldehyde-PP at 25 °C

Vapor	activity	0.1	0.3	0.5	0.7	0.9
D	PP resin		33.001	26.489	34.253	20.912
$[m/s]^{-12}$	PP sheet	4.873	1.001			


Figure 4.8. Comparison of solubility coefficient (S) and diffusion coefficient (D) at different vapor activities.

The solubility coefficient (S) and diffusion coefficient (D) for sorption of benzaldehyde in PP resin under the test conditions are compared and shown in Figure 4.8. The squares and triangles are the S and D values, individually. The solid lines are the linear trend lines based on the S / D values. It is found that S and D have reverse trend with increasing the vapor pressure, i.e. the higher the vapor activity, the larger the S values, but the smaller the D values. This interesting phenomenon indicates the structural changes within the polymer may occur, such as relaxation effects of the polymer side chains, free volume variations or swelling of the materials, especially at high vapor activities. The crystalline zones might also contribute to the changes by reducing and restraining the polymer chain mobility in the amorphous region because the chain ends are trapped in the neighboring crystalline lamellae, and then lead to higher activation energy of diffusion. That might explain the fact we observed that at high vapor activities (0.7-0.9), where the relaxation likely happened, the lower the *D* values were found. The exact reason will require future study.

4.4 Conclusion

The sorption of benzaldehyde in different PP forms (resin, sheet, thermoformed sheet and atatic PP) was studied at 25 °C. A continuously gravimetric method was adopted in the sorption study by recording the weight gain of dry polymer under certain vapor pressures. It was found that both surface area, polymer bulk properties, geometry and morphology contribute to the sorption properties of polymer. The polymer processing (extrusion and thermoforming) induced surface and morphology changes during the heat treatment, thus changed the sorption of polymer dramatically. It was also found the changes in the morphology due to processing had a large impact on the sorption of benzaldehyde at high vapor activities since the sorption of benzaldehyde on the resin is much lower than that on the sheet, the thermoformed sheet and the ataic PP

It was also observed that in PP resin, as vapor activity increased, solubility coefficient (S) increased and diffusion coefficient (D) decreased.

The two-stage sorption was observed in resin at high vapor acitivities under the testing conditions. It indicates that upon vapor sorption structural changes within the polymer may occur, such as relaxational effects of the polymer side chains, free volume variations, glass transition temperature lowering and an increase in viscoelastic behavior. The experimental results demonstrated that polymer processing changed the polymer morphology and surface structure, thus had great impact on the sorption behavior, especially at high vapor pressures.

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Chapter 5

Conclusion

The organic barrier property of polypropylene (PP) was studied in this project. A gravimetric method was developed to evaluate the sorption of benzaldehyde by PP *via* a SGA100R gravimetric system including a Rubotherm magnetic suspension electrobalance. The instrument variability and noise were studied before the sorption study. The drift was observed at the test conditions varied from $2*10^{-8}$ to $3*10^{-5}$. The Noise was observed and the amplitude was in the range of 0.0124% to 0.165%.

A continuously gravimetric method was developed to study the sorbate uptake and sorption kinetics of benzaldehyde vapor in rubbery PP resin, sheet and polyhedron thermoformed container *via* SGA-100R gravimetric analyzer at 25°C, 0% RH.

Solubility coefficients for benzaldehyde sorption in PP resin, sheet and container were determined based on the equilibrium uptake. Diffusion coefficients were also calculated on PP resin and sheet in the Fickian diffusion region. Interestingly, as the vapor activity increased, the solubility coefficient increased and the diffusion coefficient decreased in benzaldehyde – PP resin system.

It was found that surface area, geometry and morphology contributed to the sorption properties of polymer. The experimental results demonstrated that polymer processing, including extrusion and thermoforming, had a great impact on the mass transfer properties of PP, especially at high vapor activities. The processing changed the polymer morphology and surface structure, thus induces the changes in organic barrier properties among different polymer forms. It was found that the sorption of benzaldehyde in the PP polyhedron container was twice that of the sorption in PP sheet at lower vapor activities, and the sorption in sheet was almost three times the sorption of the resin at higher vapor activities. The sorption dynamics of the polyhedron container, sheet and resin were found different from each other.

The results and conclusions of this work could be used to contribute to the PP mass transfer database. Current finding emphasizes the need to assess mass transfer of formed polymer sheets or containers to accurately determine the barrier properties of packaging systems.

The future work of this project includes:

- To determine how the polymer bulk property and surface property affect the sorption process and how does each factor contribute to the sorption properties.
- To compare solubility coefficient (S) and diffusion coefficients (D) in different PP forms.
- Try to determine the method to calculate *D* for attaic PP and polyhedron containers.
- To minimize the drift and noise in the SGA 100R gravimetric analyzer.

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