Formaldehyde Mass-Transfer Properties Study

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ABSTRACT

Formaldehyde, an important feedstock in industrial processes and manufacture, is widely present in numerous consumer products. Emitted by many types of consumer products and indoor materials, indoor air can contain high concentrations of formaldehyde. Exposure to formaldehyde is hazardous to human health. Thus knowledge of formaldehyde mass-transfer properties is critical to efforts to reduce formaldehyde emissions and establish related standards and regulations.

The primary objectives of this project include: 1) documenting and validating procedures and methods for analyzing and measuring formaldehyde mass-transfer characteristics; 2) evaluating and comparing formaldehyde mass-transfer properties in different materials using micro-balance sorption/desorption tests; 3) investigating observed formaldehyde mass-transfer irreversibility and the recently developed formaldehyde polymerization theory.

The procedures and methods for analyzing and measuring formaldehyde mass-transfer characteristics were developed in an effort to minimize experimental variability and were strictly followed during the research. The formaldehyde mass-transfer properties of five polymer materials (polycarbonate, polystyrene, poly(methyl methacrylate), polyethylene and polypropylene) were measured through sorption/desorption testing. Results indicated that formaldehyde solubility was highest in polyethylene while the rate of diffusion was the highest in polypropylene. Results also showed that the diffusion process in the selected polymer materials was irreversible in all cases. Furthermore, additional testing showed no detectable polyformaldehyde formation on polymer surfaces after exposure to formaldehyde. The causes of observed mass-transfer irreversibility need further study.
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**List of abbreviations**

\( A \)  exposed surface area of the material (m\(^2\))
\( A_s \)  chamber surface area that exposes to chamber air (m\(^2\))
\( C \)  material-phase concentration of formaldehyde (g/m\(^3\))
\( C_0 \)  initial uniform material-phase concentration of formaldehyde (g/m\(^3\))
\( C_1 \)  constant material-phase concentration of formaldehyde in the lower surface (g/m\(^3\))
\( C_2 \)  constant material-phase concentration of formaldehyde in the upper surface(g/m\(^3\))
\( C_s \)  VOC concentration in the air just adjacent to the interface
\( D \)  diffusion coefficient of the VOC in the material (m\(^2\)/s)
\( h_m \)  convective mass-transfer coefficient (m/h)
\( K \)  partition coefficient of the VOC between the material and air (dimensionless)
\( K' \)  so-called partition coefficient of the VOC between the material and air (dimensionless)
\( K_s \)  surface/air partition coefficient (dimensionless)
\( L \)  thickness of the material (m)
\( Q \)  volumetric air flow rate (m\(^3\)/h)
\( q \)  concentration of VOCs in the adsorbed surface (g/m\(^3\))
\( r \)  correlation coefficient
\( t \)  time (s)
\( V \)  well-mixed chamber volume (m\(^3\))
\( x \)  distance from the base of the material (m)
\( y \)  gas-phase formaldehyde concentration in the well-mixed chamber air (g/m\(^3\))
\( y_0 \)  VOCs initial concentration in the chamber air (g/m\(^3\))
\( y_{in} \)  gas-phase formaldehyde concentration in the influent air (g/m\(^3\))
\( y_{\infty} \)  gas-phase formaldehyde concentration in the gas stream going through the micro-balance (g/m\(^3\))

**Additional abbreviations**

ACH  Air change per hour
ATSDR  the Agency for Toxic Substances and Disease Registry
CEE  Civil and Environmental Engineering
DDL  Diacetyldihydrolutidine
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>DNPH</td>
<td>2,4-Dinitrophenylhydrazine</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared ray</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
</tr>
<tr>
<td>IARC</td>
<td>the International Agency for Research on Cancer</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared ray</td>
</tr>
<tr>
<td>LC/MS</td>
<td>Liquid chromatography/ mass spectrometry</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
</tr>
<tr>
<td>NIST</td>
<td>the National Institute of Standards and Technology</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PRA</td>
<td>Pararosaniline</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>QAPP</td>
<td>Quality assurance project plan</td>
</tr>
<tr>
<td>SBIO</td>
<td>Sustainable Biomaterials</td>
</tr>
<tr>
<td>SVOCs</td>
<td>Semi-volatile organic compounds</td>
</tr>
<tr>
<td>U.S. EPA</td>
<td>the Unites State Environmental Protection Agency</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>VT</td>
<td>Virginia Tech</td>
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<tr>
<td>WBC</td>
<td>Wood Based Composites Center</td>
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1. Introduction

A colorless, flammable gas with an irritating odor at room temperature, formaldehyde is a chemical feedstock for various industrial processes and is widely used in the production of building materials, household products and resins for wood products (the Agency for Toxic Substances and Disease Registry (ATSDR), 2009; Salthammer et al., 2010; US EPA, 2006). In addition, formaldehyde is an important component of germicides, fungicides, insecticides and preservatives (Musterman, 1977; Passman, 1996; Rosenkranz, 1972). Formaldehyde is widely present in numerous consumer products, such as antiseptic, cleaning agents, carpet, cigarettes, cosmetics, fertilizers, insulation for electrical uses, manufactured wood products, medicines, paints and preserved food, and can be emitted from these products (ATSDR, 2009; Pilato, 2010; Lefebvre et al., 2012). Formaldehyde is therefore often found at high concentrations in indoor air (Tang et al., 2009).

Formaldehyde is hazardous to human health. Formaldehyde at concentrations above 0.1 parts per million (ppm) can cause difficulty in breathing, irritation of the eyes, nose, throat, nausea and lungs, and induce asthma (Salthammer et al., 2010; US EPA, 2006). Formaldehyde is also classified as human carcinogen (IARC, 2006; Rosenkranz, 1972; US EPA, 2006). Humans formaldehyde exposure pathways include respiratory, dermal, and ingestion. (ATSDR, 2009).

Due to the adverse health effects associated with formaldehyde exposure, formaldehyde has been identified as one of the most serious hazardous by the U.S. Environmental Protection Agency (US EPA, 2006). Some organizations and countries established formaldehyde exposure standards in efforts to reduce human health risks. For example, Germany and Singapore have established a maximum formaldehyde exposure concentration of 0.1 ppm, in indoor air (Tang et al., 2009). Improved knowledge of formaldehyde mass-transfer properties and reaction pathways could help reduce formaldehyde emissions and guide the establishment of effective standards and regulations.

Standards development and implementation would also be facilitated by the availability of a formaldehyde emissions reference material. Such a reference material could be used to validate chamber testing results. Currently chamber validation is done through inter-laboratory studies that are costly, and time-consuming, and do not provide insight as to sources of variability. In
previous efforts to develop a formaldehyde emissions reference material using polycarbonate (PC) films, formaldehyde mass-transfer irreversibility was encountered. Determining the cause of the observed irreversibility would facilitate further development of a formaldehyde emissions reference material and is an important objective of this research project.

However, formaldehyde mass-transfer properties and reaction pathways are not currently fully understood. Previous efforts to develop PC film as a reference material for formaldehyde emissions testing found that formaldehyde mass-transfer was not completely reversible.

In addition, the laboratory methods and procedures for measuring diffusion-based mass-transfer properties have not been thoroughly documented and validated.

With the funding provided by Wood Based Composites Center (WBC), researchers at Virginia Tech (VT) have documented laboratory procedures for evaluating formaldehyde mass-transfer properties and have used gravimetric methods to measure the mass-transfer properties of formaldehyde in five polymer materials, PC, polystyrene (PS), poly(methyl methacrylate) (PMMA), polyethylene (PE) and polypropylene (PP). In addition the possibility of formaldehyde mass-transfer irreversibility due to polymerization on surfaces was investigated using fluorimetric and Fourier transform infrared (FTIR) spectrometric methods. These tests produce no evidence of polymerized formaldehyde on materials surfaces.

To summarize, the goals of this project include: 1) documentation and validation procedures and methods for analyzing and measuring formaldehyde mass-transfer characteristics; 2) evaluation and comparison formaldehyde mass-transfer properties in five different materials using micro-balance sorption/desorption testing; 3) investigation observed formaldehyde mass-transfer irreversibility and the recently developed formaldehyde polymerization theory.
2. Literature review-formaldehyde mass-transfer models, properties, and estimation method

2.1 Introduction
As formaldehyde can adversely affect human health, it is imperative that actions to limit formaldehyde emissions are taken (Salthammer et al., 2010; US EPA, 2006). However, formaldehyde mass-transfer properties and chemical reaction pathways are not yet fully understood. The objective of this project was to investigate formaldehyde mass-transfer properties and potential chemical reactions.

Formaldehyde is emitted from many indoor materials and is classified as a volatile organic compound (VOC) by some organizations (Missia, et al., 2010). The VOC mass-transfer models that have been developed and improved during the past decades can therefore be applied to formaldehyde. Crank’s model describing VOC diffusion through a homogeneous material and Little’s model describing VOC emissions from a homogeneous layer of polymer material are two widely used models that can be used to investigate formaldehyde mass-transfer properties (Crank 1979; Little, et al., 1994).

In addition to mass-transfer properties, investigation is needed to explore formaldehyde chemical properties especially polymerization as there is little available knowledge on this subject (Machacek et al., 1961; Walker, 1953). Analytical methods such as colorimetry, gas chromatography (GC), high-performance liquid chromatography (HPLC), ultraviolet–visible spectrophotometry, and FTIR spectroscopy can be used to detect and quantify formaldehyde and polyformaldehyde and are important for formaldehyde polymerization study (Bricker et al., 1945; Cares, 1968; Cinti et al., 1977; Eckmann et al. 1982; Fagnani et al., 2003).

In this review, the current understanding of VOC/formaldehyde mass-transfer and the properties of formaldehyde is summarized. Different techniques used to detect and quantify (poly)formaldehyde are also summarized and compared.
2.2 Formaldehyde mass-transfer models

2.2.1 VOCs/Formaldehyde diffusion model

The diffusion of VOCs/formaldehyde through a pure and homogeneous material is described by Fick’s second law, the model describing VOCs diffusion through a plane sheet was presented by Crank (1979).

![Idealized schematic representation of VOC diffusion through a plane sheet with different surface concentrations](image)

**Figure 2.1** Idealized schematic representation of VOC diffusion through a plane sheet with different surface concentrations

An idealized schematic representation of uniform initial VOC distribution through a plane sheet with different surface concentrations is shown in Figure 2.1. The boundary conditions assume that concentrations in upper and lower surfaces are constant with time, or

\[
C(x = 0, t) = C_1, \quad t \geq 0 \tag{2.1.1}
\]

\[
C(x = L, t) = C_2, \quad t \geq 0 \tag{2.1.2}
\]

where \(C(x, t)\) is the material-phase VOCs/formaldehyde concentration in the polymer slab, \(t\) is time, \(x\) is the linear distance from the bottom of the slab, and \(C_1\) and \(C_2\) are VOCs/formaldehyde concentrations in upper and lower surfaces. And the initial condition assumes that the slab is initially at a constant concentration, or

\[
\frac{\partial^2 C}{\partial x^2} = 0 \tag{2.1.3}
\]

The diffusion coefficient \(D\) is constant, or

\[
\frac{\partial C}{\partial t} = a \tag{2.1.4}
\]

where \(a\) is a constant. The solution for equations (2.1.1) - (2.1.4) could be obtained by Laplace’s transformation, or

\[
C = C_1 + (C_2 - C_1) \frac{x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{L} \exp(-\frac{Dn^2\pi^2 t}{L^2}) +
\]
\[
\frac{4C_0}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \left( \frac{(2m+1)\pi x}{L} \right) \exp \left\{ -\frac{D(2m+1)^2\pi^2 t}{L^2} \right\}
\]
(2.1.5)

Where \( L \) is the thickness of material, \( C_0 \) is the initial uniform formaldehyde concentration in the material slab. This equation could also be expressed by the total mass of diffusing substance entering the slab during a period of time, or
\[
\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left\{ -\frac{D(2n+1)^2\pi^2 t}{L^2} \right\}
\]
(2.1.6)

where \( M_t \) is the total mass of the diffusion substance that enters the slab during time \( t \), \( M_{\infty} \) is the total mass of the diffusion substance that enters the slab during infinite time.

This model assumes that the material slab is thin enough so that the diffusion substance enters the slab through the plane faces, and the amount entered through edges is negligible.

### 2.2.2 VOCs/Formaldehyde emission model

The VOCs/semi-volatile organic compounds (SVOCs) mass-transfer model widely used nowadays has been progressively developed and improved over the past few decades. The early diffusion model derived by Little, et al (1994) laid the ground work for later mass-transfer models.

![Figure 2.2](image)

**Figure 2.2** Idealized schematic representation of VOC diffusion from a homogeneous polymer material with external convective mass-transfer resistance ignored
Figure 2.2 shows an idealized schematic representation of VOC diffusion from a homogeneous layer of polymer material (Little, et al., 1994). The governing equation describing transient diffusion through the polymer is Fick’s second law, or

\[
\frac{\partial C(x,t)}{\partial t} = D \cdot \frac{\partial^2 C(x,t)}{\partial x^2} \tag{2.2.1}
\]

The initial condition assumes that the VOC is uniformly distributed throughout the slab, or

\[
C(x, t = 0) = C_0 \ (0 \leq x \leq L) \tag{2.2.2}
\]

The first boundary condition assumes that there is no flux on the bottom of the polymer slab, or

\[
\frac{\partial C(x=0,t)}{\partial x} = 0 \tag{2.2.3}
\]

The gas-phase VOC concentration in influent air is assumed to be zero \((y_{in} = 0)\). A second boundary condition on the top surface is imposed through a mass balance on the VOC in the well-mixed chamber air, or

\[
\frac{\partial y(t)}{\partial t} \cdot V = -D \cdot A \frac{\partial C(x=L,t)}{\partial x} - Q \cdot y(t) \tag{2.2.4}
\]

where \(y\) is the VOC concentration in the chamber air, \(Q\) is the volumetric flow rate of air through the chamber, \(V\) is the volume of air in the chamber, and \(A\) is the slab surface area that exposes to chamber air. Equilibrium is assumed to exist between the VOC concentrations in the slab surface layer of the polymer and the chamber air, or

\[
K = \frac{C(x=L,t)}{y(t)} \tag{2.2.5}
\]

where \(K\) is the partition coefficient between VOC centration in the polymer material and in the chamber air. The solution for equations (2.1) – (2.5) is

\[
C(x,t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp\left(-Dq_n^2t\right) \left(h-kq_n^2\right) \cos(q_nx)}{\left[h-kq_n^2\right] + q_n^2h + h} \cos(q_nL) \right\} \tag{2.2.6}
\]

where

\[
h = \frac{Q/A}{D \cdot V} \tag{2.2.7}
\]

\[
k = \frac{V/A}{K} \tag{2.2.8}
\]

And \(q_n\)'s are the positive roots of

\[
q_n \tan(q_nL) = h - kq_n^2 \tag{2.2.9}
\]

This model assumes that both \(D\) and \(K\) are independent of VOC concentration. Chamber sink effect and external convective mass-transfer resistance between the material surface and the well-mixed air in the chamber are assumed to be negligible.
Figure 2.3 Idealized schematic representation of VOC diffusion from homogeneous polymer material considering chamber sink effect

In reality, the chamber surface could also sorb VOC, in order to describe the chamber sink effect, a reversible linear equilibrium relationship is assumed to exist between chamber inner surface and the chamber air, as shown in Figure 2.3 (Cox et al., 2002), or

$$K_s = \frac{q}{y}$$

(2.2.10)

Where $q$ is the concentration of VOCs in the adsorbed surface, $K_s$ is the surface/air partition coefficient, $A_s$ is the chamber surface area that exposes to chamber air. Assuming the VOCs concentration in the influent air is zero the mass balance of VOCs in the chamber can be obtained, or

$$\frac{\partial q}{\partial t} A_s + \frac{\partial y}{\partial t} V = -Qy$$

(2.2.11)

combining equations (2.2.10) and (2.2.11), a integrating results could be obtained, or

$$ln\left(\frac{y}{y_0}\right) = -\left(\frac{q}{V+K_s A_s}\right) t$$

(2.2.12)

Where $y_0$ is the initial VOC concentration in the chamber air.
As mentioned before, the models above assume that the external convective mass-transfer resistance between the material surface and the well-mixed air in the chamber are small and negligible. A third boundary condition is considered on the top surface of the slab to describe the external convective mass-transfer resistance between the materials surface and the well-mixed air the chamber, as shown in Figure 2.4 (Xu, et al., 2003), or

\[-D \frac{\partial C(x=L,t)}{\partial x} = h_m (C_s(t) - C_\infty(t)), \quad t > 0 \]  (2.2.13)

where \(h_m\) is the convective mass-transfer coefficient, \(C_s(t)\) is the VOC concentration in the air just adjacent to the interface, \(C_\infty(t)\) is the VOC concentration in atmosphere. Equilibrium is assumed to exist between the VOC concentrations in the slab surface layer of the polymer and the ambient air, or

\[K' = \frac{C(x=L,t)}{C_s(t)} \]  (2.2.14)

where \(K'\) is the so-called partition. The solution of equations (2.2.1) − (2.2.3), (2.2.13) − (2.2.14) is:

\[C(x,t) = KC_\infty(t) + \sum_{m=1}^{\infty} \frac{\sin(\beta_m L)}{\beta_m} \frac{2(\beta_m^2 + H^2)}{L(\beta_m^2 + H^2)} \cos(\beta_m x) \times \left[ (C_0 - KC_\infty(0))e^{-D\beta_m^2 t} + \int_0^t e^{-D\beta_m^2 (t-\tau)} KdC_\infty(\tau) \right] \]  (2.2.15)

where \(H = h_m/KD\), \(\beta_m\) (m=1,2,...) are the positive roots of \(\beta_m \tan(\beta_m L) = H\)  (2.2.16)
2.3 Formaldehyde properties
Formaldehyde is usually kept in the form of Formalin, an aqueous solution containing 37% formaldehyde and proper amount of methanol to prevent emissions and polymerization (Walker, 1953). Studies show that temperature and humidity could affect formaldehyde mass-transfer properties, that is, formaldehyde has different emission rates at different temperatures or different humidities (Hennebert, 1988; Parthasarathy et al., 2011; Wiglusz et al., 2002; Xu et al., 2012). In addition to temperature and humidity, formaldehyde also has different mass-transfer properties in different polymer materials, such as plasticized polyvinyl chloride (PVC), polyoxymethylene, PC, PS, PMMA, PP and unplasticized PVC (Hennebert, 1988). Previous study found that surface coating or laminates could help to reduce formaldehyde emissions (Barry et al., 2006). Usually, formaldehyde specific emission rate increases as formaldehyde content in material increases (He et al., 2012). Except for diffusion, formaldehyde could also react with some materials, such as cellulose, paper, latex rubber and nylon (Walker, 1953).

Pure formaldehyde would not polymerize at temperatures at 80 to 100 ºC, however, water could act as transfer agent in formaldehyde polymerization, the molecular weight of polymer decreases with increase of humidity (Macháček et al., 1961; Walker, 1953). Formaldehyde could also polymerize when catalyst is present, such as hydrogen chloride, boron trifluoride and stannic chloride (Bevington et al., 1951). Polyformaldehyde may exist in various forms, such as chain polymers and cyclical polymers. Paraformaldehyde, a white solid with pungent odor, is the only formaldehyde polymer being produced for industry use (Gooch, 2007; Walker 1953). It is a low weight linear polymer of formaldehyde, contains 8-100 formaldehyde units per molecule, and can depolymerize into monomer formaldehyde when mildly heated in dry condition (Walker, 1953).

2.4 Formaldehyde estimation methods
Due to the adverse effect to human health, to accurately measure formaldehyde mass is important for formaldehyde study and detection. The estimation methods should be sensitive, accurate and easy. Usually, formaldehyde mass is hard to be directly estimated, however, formaldehyde could be indirectly estimated by the product of reaction between formaldehyde and other reactants due to its high reactivity and solubility in aqueous solutions (Grutzner et al., 2004, Walker, 1953).
In the presence of sulfuric acid, formaldehyde dissolved in water could react with chromotropic acid to form purple complex at high temperature (Bricker et al., 1945). The formaldehyde mass could then be measured by visible absorption spectrometry method at a wavelength of 570 – 580 nm (Bricker et al., 1945; NIOSH 3500, 1994). The colorimetric method is easy to operate and is also recommended by NIOSH as a standard method to determine formaldehyde between 0.02 ~ 4 ppm in air samples (NIOSH 3500, 1994). However, the method could be disturbed by other substance, such as phenol, dissolved oxygen, and oxides of nitrogen (Cares, 1968; Fagnani et al., 2003; Hakes et al., 1984).

Formaldehyde could also be determined by estimation of hydrazine derivatives, as formaldehyde could also react with 2,4-Dinitrophenylhydrazine (DNPH) in an acidic solution to form stable hydrazine derivatives (Lipari et al., 1982). To be analyzed, these derivatives should be first removed from the acidic solution by filtration and extraction, then evaporated to dryness, and finally diluted in a solvent for GC or HPLC analysis (Lipari et al., 1982). It works for formaldehyde concentration below 3.0 ppm in air samples (NIOSH 2016, 2003; NIOSH 5700, 1994). The advantage of this method is the high stability of reagents and samples, generally, the hydrazine derivatives could keep stable for at least two weeks at room temperature (Lipari et al., 1982). Besides, this method has a good performance for formaldehyde analysis. Nonetheless, the method is more complicated than colorimetric method (van Leeuwen et al., 2004). Furthermore, the test results could be interfered by ozone and nitrogen dioxide (Arnts et al., 1989; Karst et al., 1993; Smith et al., 1989).

When catalyzed by acid, formaldehyde could also react with pararosaniline (PRA) to form a Schiff’s base, which then could react with sulfite to form a purple chromate (Eckmann et al, 1982). Formaldehyde is determined by spectrophotometric detection of purple chromate at 570 nm wavelength (Muñoz et al., 1989). Despite that the PRA analysis could be disturbed by sulfur dioxide, this method is sensitive precise, and easy to use (Miksch et al, 1981; Eckmann, 1982).

Diacetyldihydrolutidine (DDL), which has a yellow color, could be produced when formaldehyde is add to solutions of acetylacetone and ammonium salt, this reaction is called Hantzsch reaction
DDL could be measured by spectrophotometric and fluorimetric methods (Belman, 1963; Cinti et al., 1977; Nash, 1953). Strong oxidizing agents could destroy DDL, and daylight could cause fading (Nash, 1953), the Hantzsch reaction could also be interference by some naturally occurring compounds, such as oxaloacetate and acetoacetate in the presence of magnesium ion (Cinti et al., 1977). However, this method is quick and sensitive (Reche et al., 2000).

In addition to formaldehyde, detection of polyformaldehyde is also significant to investigate formaldehyde properties. FTIR spectroscopy, a fast, accurate, sensitive spectrometer based on FTIR light after interference, could be employed to directly identify the polymers on the film surface (Dole et al., 2011; Horstman et al., 1984). The instrument is consisted by five parts: an interferometer, a fixed mirror, a movable mirror and abeam splitter (Dole et al., 2011; Vij, 2006). As shown in Figure 2.5, a beam of radiation emitted by a source is split in two equal beams, one beam is reflected to the movable mirrors while the other beam transmitted to the fixed mirror, the beams reflected by two mirrors return to the beam splitter, recombine and interfere to form constructive interference or destructive interference depending on the location of movable mirror, and is recorded by the detector (Dole et al., 2011; Vij, 2006). Normally, at characteristic resonant frequencies of the sample molecule, the radiation absorbed will result in a series of peaks in the spectrum, which then can be used to identify the sample (Vij, 2006). The special functional group of polyformaldehyde, C-O-C, can be used as the symbol to detect polyformaldehyde (Figure 2.6). The major peaks due to polyformaldehyde C-O-C stretch absorption are at wave numbers of 1098 cm\(^{-1}\), 936 cm\(^{-1}\) or 900 cm\(^{-1}\) (Lobo et al., 2003). The advantages of FTIR are high energy throughput, multiplexing, and high precision in frequency measurement while the disadvantage is that an interferogram is produced first rather than a spectrum in the interferometer (Vij, 2006).
2.5 Discussion and conclusions

VOC/SVOC mass-transfer properties and parameters could be estimated by Crank’s sorption/desorption model and Little’s emission model. These two methods are essentially the same as they both follow Fickian second law. However, the difference is that Crank’s model describes VOC diffusion through a homogeneous material and Little’s model describes VOC emissions from a homogeneous layer of polymer material. In this study, the formaldehyde mass-transfer properties could be investigated by sorption/desorption test following Crank’s model. In the designed experiment, a polymer film is hung to a micro-balance, during the sorption the clean film is passed by air containing formaldehyde, and during the desorption the film containing
formaldehyde is passed by clean purge air. The mass change of the film during sorption/desorption is recorded by micro-balance to get sorption/desorption curves and compare to Crank’s model to estimate formaldehyde mass-transfer parameters. Both of the film surfaces expose to air during actual sorption/desorption testing, the “thickness” of the film $L$ in the model therefore should be half of the actual film thickness.

Polymerization of formaldehyde at room temperature and dry conditions has not been fully understood as there are few efforts on it. However, knowledge of polymerization of formaldehyde is essential to formaldehyde mass-transfer properties study. Polyformaldehyde could be measured by FTIR spectrometry using C-O-C function group. The test results of FTIR spectrometry can directly determine the potential existence of polyformaldehyde after exposure to formaldehyde. In addition to gravimetric method, Hantzsch reaction of formaldehyde with acetylacetone and ammonium salt provides an easy and fast method to determine formaldehyde mass in addition to gravimetric method by micro-balance.

2.6 References


Chemical Reviews, 110(4), 2536-2572.
3. **Standard procedures of reference material preparation methods**

3.1 **Abstract**
A series of experimental operations were involved in investigating the mass-transfer properties of formaldehyde, such as controlling the temperature, preparing substrate films, weighing samples, generating gaseous formaldehyde, and loading formaldehyde into polymer films. As proper experimental operations could effectively reduce experimental errors, specific standards of experimental operations could help minimize the experimental variability and improve the efficiency. And the standard procedures could serve as the quality assurance project plan (QAPP) for this study as well.

The standard procedures of reference material preparation methods gave a specific description of operation procedures for generating gaseous formaldehyde, preparing substrate material films, conducting sorption/desorption test; model fit, and sample package and shipment. All of the experimental operations should follow these standard procedures.

3.2 **Introduction**
A series of experimental operations were involved in investigating the mass-transfer properties of formaldehyde, such as controlling the temperature, preparing substrate films, weighing samples, generating gaseous formaldehyde, and loading formaldehyde into polymer films. As proper experimental operations could effectively reduce experimental errors, specific standards of experimental operation were important to minimize the experimental variability and improve the efficiency. In order to avoid operational errors without strict regulations, the procedures were documented. Operators were required to wear powder-free gloves during whole operations to prevent interference caused by direct human body touching, such as disturbance of pollution and water on human hands.

The purposes of this study include:
1) standardize the experimental operations and provide reference for accuracy and proper operations;
2) serve as the QAPP for the study of investigating formaldehyde mass-transfer properties;
3) avoid operational errors and minimize the experimental variability.
3.3 Reference material preparation methods and procedures

3.3.1 Generating gaseous phase formaldehyde

Gaseous formaldehyde could be generated by heating solid paraformaldehyde (97%, Alfa Aesar, Ward Hill, MA) in a diffusion vial inside temperature-controlled chamber within a calibration gas generator (Dynacalibrator Model 190, VICI Metronics Inc., Santa Clara, CA) (Cox et al., 2001; Macháček, 1961). A clean air (UN1002, Airgas Inc., Radnor, PA) flow at 0% relative humidity and regulated by a mass-flow controller (Model FC-280S, Tylan General, Carson, CA) was passed through the chamber of the calibration gas generator (Figure 3.1). Paraformaldehyde in the diffusion vial depolymerizes to monomers and volatilizes at the elevated temperatures (Helander, 2000) and then diffuses into the purge air flow. The concentration of formaldehyde in the purge air flow is dependent on the formaldehyde emission rate from the diffusion vial and the purge air flow rate.

Figure 3.1 Gas-phase formaldehyde generating system
Clean dry air. As shown in Figure 3.2, the air supply system consists of compressed air cylinders (1, 4: connector; 2, 5: switching valve), triple valves (7, 8), air cylinder connectors (3, 6), pressure regulator knob (9), air pressure gauge for air cylinder (10), air pressure gauge for air flow (11), mass-flow controller (12), and air tubing. Compressed air in one tank can be used for about ~ 6 days at a flow rate of 250 ml/min. A smooth transition to a new tank is required before air depletion to avoid fluctuations in flow rate which could disturb the stability of the system. The steps to replace an empty air cylinder include: 1) connect 1 to 3; 2) close 5; 3) slowly twist open 7 while closing 8; 4) slowly open 2 and adjust 9 to keep the needle of 11 pointing to 10 ~ 15 psi in order to minimize the flow rate fluctuation; 5) Disconnect 6 from 4.

Figure 3.2 Air supply system

Air tubing. Polytetrafluoroethylene (PTFE), also known as Teflon, is a synthetic polymer of teferafluoroethylene and is white solid with a density of about 2200 kg/m3 at room temperature (Gooch, 2007). PTFE has a high melting temperature of 326-327 °C and is inert to most of the chemicals, except for alkali metals and highly reactive fluorinating agents (Gooch, 2007; Jordan et al., 2007). In addition, PTFE has a low coefficient of friction on most of surfaces and good dielectric properties (Gooch, 2007; Jordan et al., 2007; Khatipov et al., 2009). PTFE is widely used in research applications due to its inertness and ease of use (Rae et al., 2004). In this research, PTFE tubing with an inside diameter of 1/16 inch and an outside diameter of 1/8 inch
(Cole-Parmer, Vernon Hills, IL) was used as flow path material in some applications.

**Gaseous formaldehyde.** Two calibration gas generation systems were employed to generate formaldehyde-containing air streams. As the opening of the diffusion vial is small, a funnel is employed to add paraformaldehyde into the vial in order to avoid spilling (Figure 3.3(a)). Gently shake the vial to uniformly distribute paraformaldehyde and adjust the surface of paraformaldehyde flat before placing the vial into the oven in the horizontal position (Figure 3.3(b)).

![Figure 3.3 Diffusion Vials: (a) adding paraformaldehyde into diffusion vial; (b) paraformaldehyde evenly distributed in the vial](image)

Figure 3.4 shows the front view of the Dynacalibrator system which consists of a temperature-controlled oven, temperature controls, and fittings for tubing connections. The purge air goes into the oven through the gas inlet, mixes with monomer formaldehyde released in the oven, and then exits through the gas outlet. Press and hold the button, and use or button to set temperature. The real-time oven temperature is shown on the display when the buttons are released. Unscrew the black lid to open the oven, gently insert the vial filled with paraformaldehyde into the oven horizontally using tweezers (being careful to not spill paraformaldehyde powder out of the vial), and then firmly replace the screw cap to seal the oven.
3.3.2 Determine gas phase formaldehyde concentration

The concentration of formaldehyde in the air flow is dependent on the formaldehyde emission rate when the purge air flow rate is constant. The gas-phase formaldehyde concentration can be derived by dividing the formaldehyde emission rate by air flow rate. The emission rate of formaldehyde can be controlled with oven temperature or the vial diffusion path length or diameter.

**Paraformaldehyde emission rate.** One Mettler analytical balance (Mettler H54, Mettler-Toledo Inc., Columbus, OH) is employed in the lab to measure the weight of the diffusion vials. The maximum capacity is 160 g and the degree of accuracy is 0.01 mg. The front view of the mechanical balance is shown in Figure 3.5, and the detail view of the readout panel, which displays the weight of sample, is shown in Figure 3.6. There are three arrestment levels of the balance scale 0, 1/2 and 1. The weight pan must be clean, and all of the knobs should be turned to zero positions before weighing. To calibrate at 0 point, turn arrestment level to position 1, and line up the zero line with the pointer using the zero adjustment knob and then turn arrestment level back to position 0.
Figure 3.5 Illustration of analytical balance
The procedure of the analytical balance operation includes: 1) connect the system to the power; 2) open the chamber door and place the sample on the center of weighing pan and close the chamber door; 3) turn arrestment level to 1/2 position; 4) turn the 10 g weight control knot clockwise and watch the numbers on optical scale, when the number disappears, turn the weight control knob back one; 4) repeat the step 3 for 1 g and 0.1 g weight control knobs; 5) turn arrestment level to 1 position; 6) turn the digital counter knob counterclockwise until the next lower scale division in centered in the slot of the pointer; 7) read the result on the panel; 8) arrest the balance; 9) turn all of the knobs to zero position; 10) take the sample out of the weighing pan; 11) close chamber door.

**Air flow rate.** The air flow rate is kept constant by using a mass-flow controller. The flow rate is regulated by adjusting the input voltage value from the LabVIEW program on the monitoring computer. Air flow rate is measured by a bubble flowmeter (mini-Buck Calibrator, A.P. BUCK Inc., Orlando, FL). As shown in Figure 3.7, when air goes into the flowmeter, the liquid soap in the bottom will produce floats up the channel at a rate equal to the air flow rate. Two fixed position detectors determine the time required for the bubble to travel up the channel and the instrument derives the flow rate by dividing the volume swept by the bubble between the two detectors by the elapsed time. The air flow rate should be measured both before and after each
The steps for measuring the air flow rate are: 1) remove both port plugs and use a dropper to add a small amount of liquid soap into the meter through air inlet; 2) connect the air tube/pipe to the air inlet port; 3) press “ON” button and then press the spring button; 4) read the result shown on the panel, the unit is cm³/min; 5) repress the spring to get a mean value of duplicate detections, or repress both “ON” button the spring to get a new value; 6) press “OFF” button after usage; 7) disconnect the air tube/pipe from the Buck Calibrator and replace the port plugs.

3.3.3 Micro-balance sorption/desorption test
During a sorption/desorption test, the film is put in a glass chamber where the film weight is continuously measured using a high-resolution (0.1 μg) dynamic recording micro-balance with a
range of 0 ~ 200 mg (Thermo Cahn D-200, Thermo Fisher Scientific, Waltham, MA), as shown in Figure 3.8. During the sorption test, formaldehyde in the air flow diffuses into the material when passing by the film, and the mass gain of the film with time is recorded to generate a sorption curve. Purge air can then be passed through the film once the film has reached sorption equilibrium with the gas-phase formaldehyde to create a desorption curve. The micro-balance data is used to determine when material-phase/gas-phase equilibrium is reached. Furthermore, equilibrium formaldehyde concentration in the loaded films, $C_0$, can be obtained from the micro-balance data, by dividing the final measured mass of formaldehyde infused into the film by the film sample volume.

![Figure 3.8 Micro-balance system](image)

Prepare the films with certain dimension. Paper cutter (RT-200 Rotary Paper Trimmer, CARL manufacturing USA, Inc., Elk Grove Village, IL) and punches are employed to cut films into required dimensions. Paper cutter is used to cut film into large rectangle pieces (> 5 cm), while punch is used to cut film into a certain dimension and shape.

Micro-balance calibration. Calibration of micro-balance is important to ensure the accuracy of the experiment. Calibration is generally required once per month. Two interfaces are used in micro-balance calibration operation, as shown in Figure 3.9. Use up arrow button and down arrow button to move cursor and switch interfaces.
The calibration steps are: 1) remove all the samples and tare weights from the stirrups. 2) run D200-02.exe for calibration under run mode; 3) input “Y” for “TARE BALANCE” to zero the balance and repeat the operation until the displayed net value is +0.0000 mg; 4) place 100 mg tare weight on the sample pan, and wait for a while to allow the system to get stabilized; 5) input “100” for “INPUT CALIBRATION WEIGHT” and input “Y” for “CALIBRATION BALANCE” to calibrate the balance; 6) repeat steps 5 and 6 as slowly approaching the value of the exact calibration weight. 7) place some tare weights in the right arm to reduce the net weight in case that weight of the film exceeds the maximum value.

**Micro-balance data recording and reading.** Micro-scan is a real-time display system connected to the micro-balance. The measured weight value will be transferred into signal, received and recorded by Micro-scan system. The real time data is displayed in the screen in an intuitive form — a curve showing the relationship between weight of the sample and time. MicroScan Analysis is a system for data storage. The data could also be exported as a .csv suffix document through MicroScan analysis.

The steps to use micro-scan include: 1) start MicroScan software; 2) set up a connection by choosing “Balance” in toolbar and then choose “Establish Connection” in the drop down box; 3) click “OK” on the dialog appears to confirm the command; 4) Choose “File” in toolbar and then choose “Open Method” in the drop down box; 5) set up run length and sample rate in the dialog.
appears and then click “OK” to confirm the command; 6) click “Start Run” in the dialog located at the upper right corner to start the scanning and recording; 7) choose storage path and name the document in the dialog appears, and then click “Save” to save the settings; 8) Set up X-axis and Y-axis by choosing “set up” in the drop down box of “chart” in the tool bar, input the values according to demands and click “OK” to save settings; 9) once the program is running, the main interface will appear; 10) to terminate the program, simply click “End Run” in the dialog located at the upper right corner., and choose “Yes” on the dialog appears to confirm the command.

The steps to export the data are: 1) open MicroScan Analysis program 2) choose “File” in toolbar and then choose “Open” in the drop down box; 3) choose storage path and name the document in the dialog appears, and then click “Open” to open the document; 4) choose “File” in toolbar and choose “Export” in the drop down box, then choose “Comma/Tab Separated…” in the submenu; 5) choose storage path and name the document in the dialog appears, then click “Save” to save data.

**Sorption/desorption test with micro-balance.** Cut the film and stick a tiny hole with a pin. Hang the film sample into the left arm of the micro-balance with thin stainless stain wire. Open Micro-scan to read and record the data. Before testing, the clean air should be passed through for several days to purify and dry the film.

**Film loading.** Sometimes several films are needed to be loaded with formaldehyde for analysis. As shown in Figure 3.10, films are vertically inserted in holders to make sure both sides expose to air. Holders are placed in a stainless steel chamber connected to micro-balance. Films sorbs formaldehyde when passed by air containing formaldehyde. Effluent from the chamber enters micro-balance and diffuse into the film in micro-balance. Because both the film in the micro-balance and films in the loading chamber are loaded with formaldehyde under the same conditions, the diffusion process in all films are considered identical. Data recorded by micro-balance could be used to determine when material-phase/gas-phase equilibrium was reached, and the formaldehyde mass in films.
3.3.4 Film package and shipment

The films should be specially packaged to minimize the formaldehyde loss during shipment when sent to other labs. Usually films are tightly wrapped with alum foil in several layers. All the warped films are put into dry-ice-fulfilled boxes, labelled clearly and sent to labs by FedEx overnight service.

3.3.5 Clean of experimental supplies

Experimental supplies such as stainless steel parts and glass bottles should be cleaned before use. The supplies are first cleaned with tap water, distilled water and deionized water, then rinsed several times with methanol and butyl alcohol to dissolve monomer and polymer contaminants, finally dried in a heated oven.

3.3.6 Temperature control of micro-balance

The temperature should be kept constant in order to avoid the interference of temperature change. Each micro-balance system is placed in a temperature-controlled case. Two Polystat cooling/heating recirculation chillers (Cole-Parmer Polystat recirculator-17 lpm, Cole Parmer, Vernon Hills, IL) are employed to keep the temperature stable and two fans in each case are employed to continuously stir the air and evenly distribute the temperature. 50% ethylene glycol solution is used as coolant.
3.3.7 Sorption/desorption model fit
When Fick’s diffusion controls the sorption and desorption process, $D$ can be determined by fitting a Fick’s diffusion model to sorption and desorption curves. The mass change caused by Fick’s diffusion of formaldehyde inside the film is given by (Crank, 1979):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{D(2n+1)^2\pi^2 t}{L^2}\right\}$$

(3.1)

where $M_t$ is the total formaldehyde mass that has entered or left the film via diffusion in time $t$. $M_\infty$ is the formaldehyde mass in the film when partition equilibrium between the film and the air is reached, and $L$ is the thickness of the film. As both sides of films expose to air in this study, $L$ here means the half of film thickness. $K$ can be derived by dividing formaldehyde concentration in the film, by the gas-phase formaldehyde concentration. The model sorption/desorption curve is created by MATLAB code based on equation (3.1), and is attached in Appendix.

Sorption and desorption model codes need to induce experimental data from .csv suffix document to make figures and calculate the difference between model and real data using minimum squares. To run the model, first save experimental data into the .csv suffix document: time (s) in the first column, VOC mass in the second column and $M_t/M_\infty$ in the third column. Notably, save only numbers and do not input any other characters in this document. Then input parameters in the code, such as total time, time step, thickness of film, $C_0$ and $D$ and run the model. The $D$ value could be determined by trial-and-error method. An example of figures made by MATLAB models is shown in Figure 3.11.
Figure 3.11 An example of MATLAB sorption/desorption model figure.

3.4 References


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compression. Polymer, 45(22), 7615-7625.
4. Formaldehyde mass-transfer properties study

4.1 Abstract
As formaldehyde can adversely affect human health, it is imperative that actions to limit formaldehyde emissions are taken. However, formaldehyde mass-transfer properties and chemical reaction pathways are not yet fully understood.

One objective of this project was to investigate formaldehyde mass-transfer properties and potential chemical reactions. Steps taken to accomplish this objective were: 1) select polymer substrates for formaldehyde mass-transfer/chemical reaction properties study; 2) measure formaldehyde mass-transfer properties in selected substrates through gravimetric sorption/desorption testing; 3) investigate the possibility of formaldehyde polymerization by measuring formaldehyde on the surfaces of PTFE tubing, PC film, and aluminum foil using FTIR surface analysis and fluorimetry testing.

PC, PS, PMMA, PE and PP were selected as candidate materials for the formaldehyde mass-transfer study. The diffusion parameters were determined gravimetrically by sorption/desorption testing. Results indicated that formaldehyde had the highest solubility in PE and had the highest diffusion rate in PP. Results also suggested that the formaldehyde mass-transfer process was irreversible in the selected polymer substrates. Furthermore, additional testing showed no detectable polyformaldehyde formation on the polymer surface after exposure to formaldehyde. Further study is required to investigate the cause of formaldehyde mass-transfer irreversibility.

4.2 Introduction

4.2.1 Background information
Formaldehyde is a colorless, flammable gas with an irritating odor at room temperature. It is a chemical feedstock for various industrial processes and is widely used in the manufacture building materials, household products, and resins for wood products (ATSDR, 2009; Salthammer et al., 2010; US EPA, 2006). In addition, formaldehyde is an important component in germicides, fungicides, insecticides and preservatives (Musterman, 1977; Passman, 1996; Rosenkranz, 1972). Formaldehyde is widely present in numerous consumer products, such as antiseptic, cleaning agents, carpet, cigarettes, cosmetics, fertilizers, insulation for electrical uses, manufactured wood
products, medicines, paints, and preserved food, and consequently is emitted from these materials into air (ATSDR, 2009; Lefebvre et al., 2012; Pilato, 2010). Thus, formaldehyde may exist at high concentrations in indoor air (Tang et al., 2009).

Formaldehyde is hazardous to human health. Formaldehyde at gas-phase concentrations above 0.1 parts ppm can cause difficulty in breathing, burning sensations in the eyes, nose, throat, and lungs, and induce asthma (Salthammer et al., 2010; US EPA, 2006). Formaldehyde is also classified as carcinogenic to humans (IARC, 2006; Rosenkranz, 1972; US EPA, 2006). Humans can be exposed to formaldehyde by breathing air containing formaldehyde, dermal contact with liquid containing formaldehyde, or ingesting formaldehyde in food or water (ATSDR, 2009).

Due to the adverse health effects associated with formaldehyde exposure, formaldehyde has been included in the list of hazardous air pollutants by the U.S. Environmental Protection Agency (US EPA, 2006). Some organizations and countries have established maximum indoor gas-phase formaldehyde concentration in efforts to reduce human health risks. For example, the International Agency for Research on Cancer (IARC), Germany and Singapore suggest a maximum formaldehyde exposure limit of 0.1 ppm (Tang et al., 2009). Knowledge of formaldehyde mass-transfer characteristics is a critical requirement in the efforts to establish effective standards and regulations for formaldehyde exposure.

However, the mass-transfer properties of formaldehyde are not currently fully understood. Previous efforts to develop a PC film as reference material for formaldehyde emissions testing found that the formaldehyde diffusion process was not fully reversible. A possible explanation put forth by the researchers was that polymerization of formaldehyde could be occurring on the surface of the PC film. However, the theory lacks sufficient evidence. Further study of formaldehyde mass-transfer properties and creation of a well-characterized reference material for formaldehyde emissions testing is therefore critical for formaldehyde evaluation and regulation.

The process of this phase of the research project consisted of the following steps: 1) choose several polymer substrates for formaldehyde mass-transfer properties study; 2) investigate formaldehyde mass-transfer properties in selected substrates by micro-balance sorption/desorption testing; 3)
investigate the theory of formaldehyde polymerization on surfaces through fluorimetric and FTIR spectrometric analysis.

4.2.2 Objectives
The specific objectives of this research project were to:
1) evaluate and compare formaldehyde mass-transfer process in several polymer films;
2) measure the diffusion coefficient, $D$, and partition coefficient, $K$, of formaldehyde in each of the selected polymer films;
3) evaluate formaldehyde polymerization theory by searching for evidence of polyformaldehyde formation on the surfaces of film and other experimental substrates.

4.3 Materials and methods
4.3.1 Micro-balance sorption/desorption testing of polymer films
4.3.1.1 Selection of polymers for sorption/desorption testing
For a formaldehyde reference material the ideal polymer should be stable and nonreactive with formaldehyde. It also should be uniform and not contain any reactive or volatile impurities such as additives or contaminants that may confound mass-transfer of formaldehyde within the material. In addition, formaldehyde needs to have high solubility in the selected polymer substrates so that a measurable amount of formaldehyde can be loaded into the material. Furthermore, the diffusion of formaldehyde in the polymer substrates must be ideal Fickian in nature.

Previous study indicated that PVC, high density polyethylene (HDPE), PP, PS, PMMA, polyoxymethylene, and PC would not react with formaldehyde and would therefore be potential candidates for use as a reference material substrate (Hennebert, 1988). In this study, PC, PS, PMMA, PE and PS were chosen for study. Low density polyethylene (LDPE) was also considered as a substrate as it was more porous and therefore was expected to have a higher formaldehyde solubility than HDPE. The chemical structures of selected polymers are shown in Figure 4.1 (Gooch, 2007). These films were directly purchased from Goodfellow USA, a supplier of specialty materials for research applications.
Figure 4.1 Chemical structure of selected polymers: (a) polystyrene; (b) polycarbonate; (c) polyethylene; (d) poly(methyl methacrylate); (e) polypropylene

4.3.1.2 Generating a formaldehyde-containing gas stream

A continuous gas stream with a constant and controllable formaldehyde concentration was required to characterize the mass-transfer properties of the selected polymer films. Formaldehyde was generated by heating solid paraformaldehyde at 95 °C in a diffusion vial within a calibration gas generator with a purge air flow rate of 250 ml/min. The gas flow rate was measured using a bubble flowmeter and the formaldehyde emission rate was determined by weighing the diffusion vial on a mechanical balance each day. The linearity between the measured weight and time was examined to determine the formaldehyde emissions rate.
Previous study verified that the formaldehyde concentration in the gas stream could be accurately estimated by dividing the formaldehyde emission rate by the purge flow rate.

### 4.3.1.3 Formaldehyde sorption/desorption testing

As previously described, PC film with a thickness of 0.025 cm, PS film with a thickness of 0.019 cm, PMMA film of a thickness of 0.025, PE film with a thickness of 0.020 cm and PP film with a thickness of 0.027 cm were chosen as candidate substrates. For evaluation of formaldehyde mass-transfer properties, film samples were cut from the original sheets into 3.6 cm×3.6 cm pieces using a square punch. Films were then placed inside the glass chamber of a high-resolution (0.1 μg) recording micro-balance. The air flow rate was maintained at approximately 250 ml/min while the glass chamber volume was 560 ml, resulting in an air change per hour (ACH) of 26.78 h⁻¹. Films were purified with clean, dry, purge air for 4 ~ 5 days before being exposed to a gas stream containing a known formaldehyde concentration. After reaching sorption equilibrium clean air was passed through the glass chamber until sorption equilibrium had been re-established with the clean air. The weight of each sample was recorded every five minutes during the sorption/desorption cycles. All the tests were conducted at 25 ºC, 0% humidity.

A desorption test was conducted at higher temperature (40 ºC) to investigate the effect of temperature on formaldehyde mass-transfer properties. A PC film was first loaded with formaldehyde at 25 ºC as described above. However, the chamber temperature was increased to 40 ºC during the following desorption test.

\[ K = \frac{C_0}{\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left\{ -\frac{D(2n+1)^2 \pi^2 t}{L^2} \right\}} \]

where \( M_t \) was the total formaldehyde mass that has entered or left the film via diffusion in time \( t \), \( M_\infty \) was the formaldehyde mass in the film when partition equilibrium between the film and the air was reached, and \( L \) is the half of film thickness. MATLAB was used to perform the curve fitting for \( D \) estimation.
4.3.2 Detection of formaldehyde polymerization on surfaces

4.3.2.1 Fluorimetry - PTFE tubing formaldehyde detection

PTFE tubing was used in some portions of the formaldehyde-containing gas stream flow path. Although PTFE is thought to sorb negligible formaldehyde, testing this assumption and searching for evidence of formaldehyde polymerizing on the surface was considered worthwhile.

In this study, both used and new tubing with the same specifications and purchased from the same vendor were evaluated for formaldehyde sorption. The new tubing had not been exposed to formaldehyde, and therefore was not expected to contain formaldehyde, while the used tubing had been exposed to gaseous formaldehyde for more than 20 months. Samples were prepared for analysis by using a tubing cutter to cut used and new PTFE tubing samples into 0.25 inch long pieces. Five pieces from each of the two groups were packaged with aluminum foil and sealed in separate glass bottles for analysis (Figure 4.2).

![Figure 4.2 Samples preparation for fluorimetry test](image)
The formaldehyde in PTFE tubing was measured using fluorimetric method. DDL which has a yellow color, is produced when formaldehyde is added to solutions of acetylacetone and ammonium salt. This reaction is called the Hantzsch reaction (Nash, 1953). The fluorescence excitation and emission spectra peaks for DDL are at 410 nm and 510 nm (Belman, 1963; Dong et al., 1987). The peaks are constant in the pH range of 5.2–6.8, sulfuric acid could be used to control pH (Sritharathikhun, 2005). Monomer formaldehyde as well as short chain polyformaldehyde are soluble in water and can be detected by this method. Before test, 1 L 10 mM H₂SO₄ solution was prepared by 533 μl sulfuric acid (Sulfuric acid ACS reagent, 95.0-98.0%, Sigma-Aldrich, Saint Louis, MO) and liquid chromatography/ mass spectrometry (LC/MS) water (Optima LC/MS, Fisher Scientific, Fair Lawn, NJ). And the 1 L the reagent solution was prepared by 150 g ammonium acetate (≥97%, Fisher Scientific, Fair Lawn, NJ), 3 ml acetic acid (≥99%, Sigma-Aldrich, Saint Louis, MO), 2 ml acetylacetone (≥99.5%, Sigma-Aldrich, Saint Louis, MO) and LC/MS water. The LC/MS water is added until the total volume of both sulfuric acid and reagent solution is 1 L. Once samples arrived at the lab, equal amounts of the H₂SO₄
solution was poured into the two glass bottles containing the PTFE samples. Each time before fluorimetry test, 4 ml of H$_2$SO$_4$ solution was extracted from each bottle and mixed with 4 ml of the reagent solution in a clean glass vial. Glass vials containing reagent solutions were placed in 60°C water bath for 10 min and were then subjected to fluorimetric measurement at a wavelength at about 510 nm. The signal emission intensity which was proportional to formaldehyde concentration in solution then could be detected to measure formaldehyde mass. Thus, the formaldehyde extracted from used and new PTFE tubing could be qualitatively compared by comparing the signal emission intensity. The fluorimetry tests were repeated until the signal intensity became stable.

To eliminate the interference of formaldehyde attached on the aluminum foil or on the glass bottle, a second PTFE test was conducted. The samples were prepared in the same condition as the first test, except for that a third group was added as background group. In the third group, only a piece of aluminum foil was placed in a blank bottle to estimate background formaldehyde. In addition, 15 pieces of PTFE tubing samples with a length of 0.25 inch were prepared in an attempt to increase the formaldehyde signal from the fluorimetry.

4.3.2.2 Fluorimetry - PS formaldehyde test

As the signal emission intensity was proportional to formaldehyde, the fluorimetry test was also utilized in an attempt to detect and quantify any formaldehyde remaining in or on the polymer film after desorption testing by comparing the signal emission intensity to the standard calibration curve. Two post-sorption test PS films and a clean PS film with the same dimension were individually packaged with aluminum foil and stored at 0 °C for two weeks. Before fluorimetry testing, a punch was used to cut ten 3.1 cm disks from each film. Disks were transferred to clean 16 mm×150 mm glass vials with caps; two disks per vial. The weight of each glass vial with and without disks was measured using an analytical balance. The sample vials were then packaged in dry ice and sent to an external laboratory for analysis. Upon arrival, 4 ml of 10 mM sulfuric acid was transferred into each vial, followed by immersion in a 90 °C water bath for one hour. After one hour in the 90°C water bath 4 ml of reagent solution was then added to each vial after cooling to room temperature. Vials were then placed in a 60 °C for 10 minutes and subjected to fluorimetry measurement. The measurements were repeated for fives until all of the samples
were measured.

The expected formaldehyde mass in the every two disks was calculated using micro-balance data. The formaldehyde mass measured by fluorimetry testing and the expected valued could be compared to determine the formaldehyde mass that could be extracted from the PS solution.

4.3.2.3 Aluminum sorption test

Aluminum is a low-density silvery white, soft, ductile metal with high thermal and electrical conductivity (Meigh, 2000; Vargel, 2004). In some conditions, a stable compact layer of oxide film can form on the surface of aluminum, as shown in Figure 4.4 and Table 4.1 (Meigh, 2000; Vargel, 2004). As shown in Table 4.1, at room temperature, only Al2O3 which is a pure impervious substance forms on the aluminum surface. Aluminum foil is impervious compared to porous polymer materials and allows little formaldehyde sorption. In addition, formaldehyde is not expected to react with either aluminum or Al2O3. Therefore, if a detectable mass increase is measured while the aluminum foil is exposed to formaldehyde, it would likely be the result of surface polymerization.

Figure 4.4 The structure of aluminum surface
<table>
<thead>
<tr>
<th>Species</th>
<th>Crystal structure</th>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Temperature range of formation (°C)</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous alumina</td>
<td></td>
<td>Aluminum Oxide</td>
<td>Al₂O₃</td>
<td>&lt;50-60</td>
<td>3.4</td>
</tr>
<tr>
<td>Bayerite</td>
<td>Monoclinic</td>
<td>Aluminum trihydroxide</td>
<td>α-Al(OH)₃</td>
<td>60-90</td>
<td>2.53</td>
</tr>
<tr>
<td>Boehmite</td>
<td>Orthorhombic</td>
<td>Aluminum Oxide hydroxide</td>
<td>γ-AlOOH</td>
<td>&gt;90</td>
<td>3.01</td>
</tr>
<tr>
<td>Corundum</td>
<td>Hexagonal</td>
<td>Aluminum Oxide</td>
<td>α-Al₂O₃</td>
<td>&gt;350</td>
<td>3.98</td>
</tr>
</tbody>
</table>

Usually, thinner film has a larger specific surface area for potential formaldehyde polymerization. However, thicker film could more effectively resist the interference of buoyancy caused by airflow. In order to take these factors into account, two different 3.6 cm × 3.6 cm aluminum foil samples of thickness 0.0005 inch and 0.002 inch were used to test for formaldehyde surface polymerization. In order to eliminate gravimetric inferences due to chemical contaminants and water, the system and aluminum foil samples were subjected to a dry purge air flow for ~ 6 days before sorption testing.

### 4.3.2.4 FTIR spectroscopy surface formaldehyde analysis

In an attempt to detect evidence of formaldehyde polymerization on surfaces, aluminum foil and PC films were subjected to FTIR analysis. Two 5 cm × 5 cm × 0.025 cm PC films were loaded with formaldehyde in a stainless steel chamber for 8 days. Before loading, films were conditioned with clean, dry, purge air for ~6 days. The formaldehyde mass in each of the two loaded PC films determined by the micro-balance method was 0.14 mg. One 3.6 cm × 3.6 cm × 0.002 cm aluminum foil was exposed to formaldehyde in the micro-balance 1 for ~ 1.5 days.
Before exposure to formaldehyde the foil samples were conditioned with clean, dry, purge air for ~ 6 days. There was no measurable mass change during the period in which the foil was exposed to formaldehyde. The loaded PC films along with an unexposed PC film of the same dimensions, and the exposed aluminum foil, along with an unexposed aluminum foil with the same dimensions were wrapped in aluminum foils, packed in dry ice, and sent to NIST by overnight delivery service for FTIR analysis.

The major infrared ray (IR) peaks for polyformaldehyde and monomer formaldehyde are summarized in the table below (Lobo et al., 2003; Clouthier, 2013).

<table>
<thead>
<tr>
<th>Table 4.2 Typical infrared absorption frequencies for (poly)formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substance</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Polyformaldehyde</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

4.4.3 Task allocation
This work was completed through the collaborative effort of three organizations; the VT Department of Civil and Environmental Engineering (CEE), the VT Department of Sustainable Biomaterials (SBIO), and NIST. This specific work completed by each organization is summarized in Table 4.3.
<table>
<thead>
<tr>
<th>Test</th>
<th>Organization/lab</th>
<th>Operator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde-PC film sorption/desorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>Formaldehyde-PS film sorption/desorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>Formaldehyde-PMMA film sorption/desorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>Formaldehyde-PE film sorption/desorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>Formaldehyde-PP film sorption/desorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>High temperature formaldehyde-PC film sorption/desorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>Aluminum-formaldehyde sorption test</td>
<td>VTCEE</td>
<td>Xiaomin Zhao</td>
</tr>
<tr>
<td>FTIR PC/aluminum surface analysis</td>
<td>NIST</td>
<td>Chiao-Chi Lin</td>
</tr>
<tr>
<td>Fluorimetry -FTIR tubing test</td>
<td>VTSBIO</td>
<td>Guigui Wan</td>
</tr>
<tr>
<td>Fluorimetry -PS test</td>
<td>VTSBIO</td>
<td>Guigui Wan;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Xiaomin Zhao</td>
</tr>
</tbody>
</table>
4.4 Results and discussion

4.4.1 Micro-balance formaldehyde sorption/desorption testing of polymer substrates

4.4.1.1 Generating formaldehyde-containing air

![Graph showing weight decrease over time for different materials](image)

**Figure 4.5** Measured weight decrease of diffusion vials over time

Formaldehyde emission rates for all sorption/desorption tests are summarized in Figure 4.5, which shows that linear weight decrease in all cases. The square of correlation coefficient (R) for all cases were larger than 0.99, suggesting that the formaldehyde emission rate is constant at a constant temperature. The formaldehyde emission rate, flow rate, and formaldehyde concentration in air flow are summarized in Table 4.2. Emission rate from a diffusion vial pathway length of 4.5 cm (circle markers) was larger than that using a pathway length of 5.5 cm (rectangle markers) when the diameter of opening is the same, showing that formaldehyde release rate increased as diffusion pathway length decreased. Data in Table 4.4 shows that the formaldehyde release rate with the same diffusion pathway length was not identical, indicating the release rate might was also affected by the content of formaldehyde in the diffusion vial.
### Table 4.4 Gaseous formaldehyde concentration

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Emission rate (g/day)</th>
<th>Flow rate (ml/min)</th>
<th>Gaseous formaldehyde concentration (g/m³)</th>
<th>Diffusion vial pathway length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>0.34</td>
<td>250</td>
<td>0.97</td>
<td>4.5</td>
</tr>
<tr>
<td>PC2</td>
<td>0.28</td>
<td>250</td>
<td>0.79</td>
<td>5.5</td>
</tr>
<tr>
<td>PS1</td>
<td>0.23</td>
<td>250</td>
<td>0.72</td>
<td>5.5</td>
</tr>
<tr>
<td>PS2</td>
<td>0.26</td>
<td>250</td>
<td>0.72</td>
<td>5.5</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.26</td>
<td>250</td>
<td>0.70</td>
<td>5.5</td>
</tr>
<tr>
<td>PE1</td>
<td>0.21</td>
<td>250</td>
<td>0.59</td>
<td>5.5</td>
</tr>
<tr>
<td>PE2</td>
<td>0.23</td>
<td>250</td>
<td>0.63</td>
<td>5.5</td>
</tr>
<tr>
<td>PP1</td>
<td>0.26</td>
<td>260</td>
<td>0.71</td>
<td>5.5</td>
</tr>
<tr>
<td>PP2</td>
<td>0.26</td>
<td>260</td>
<td>0.71</td>
<td>5.5</td>
</tr>
</tbody>
</table>

#### 4.4.1.2 Formaldehyde sorption/desorption testing

The mass gain of each film sample during each sorption/desorption test is summarized in Figure 4.6 — Figure 4.10. Data in Figure 4.6 (a), Figure 4.8 and Figure 4.9 (a) were collected by micro-balance 1 while the other data was collected by micro-balance 2.

![Figure 4.6](image-url)

**Figure 4.6** Formaldehyde-PC sorption/desorption test
Figure 4.7 Formaldehyde-PS sorption/desorption test

Figure 4.8 Formaldehyde-PMMA sorption/desorption test
As shown in Figure 4.6 — Figure 4.10, under the same conditions, different polymers sorbed different amounts of formaldehyde at different rates. For example, PP film adsorbed the least amount of formaldehyde at the highest rate while PE sorbed largest amount of formaldehyde with the lowest rate. In addition, with the exception of PE, the desorption process was faster than sorption process. In all cases, the mass of formaldehyde mass sorbed by each polymer was greater than the formaldehyde mass released from films during desorption, indicating that formaldehyde diffusion process within the set of selected polymer materials was irreversible. A possible
explanation is that some formaldehyde re-polymerized on the film surface during diffusion, which has been observed in by previous studies (Walker, 1953). However, testing conducted during the course of this project was unable to confirm the presence of polymerized formaldehyde on film surfaces. Another possible explanation is that some portion of formaldehyde in or on each film was detained in the film and could not freely release during desorption. The third possibility is that formaldehyde diffusion process in selected polymer material did not follow Fick’s diffusion law in nature. Regardless of the third possibility, the diffusion process was analyzed using Fick’s model fit, shown as lines in Figure 4.6 – Figure 4.10, $D$, $C_0$, and $K$ values are summarized in Table 4.5.

<table>
<thead>
<tr>
<th>Test film</th>
<th>Thickness (cm)</th>
<th>$D$ (sorption)</th>
<th>$K$</th>
<th>$C_0$</th>
<th>$D$ (desorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>0.025</td>
<td>$(3.9 \pm 0.49) \times 10^{-14}$</td>
<td>300±21</td>
<td>270±64</td>
<td>$(9.8 \pm 4.5) \times 10^{-14}$</td>
</tr>
<tr>
<td>PS</td>
<td>0.025</td>
<td>$(2.3 \pm 0.35) \times 10^{-14}$</td>
<td>340±49</td>
<td>240±28</td>
<td>$(4.8 \pm 3.1) \times 10^{-14}$</td>
</tr>
<tr>
<td>PMMA</td>
<td>0.020</td>
<td>$2.7 \times 10^{-14}$</td>
<td>190</td>
<td>130</td>
<td>$3.1 \times 10^{-14}$</td>
</tr>
<tr>
<td>PE</td>
<td>0.019</td>
<td>$(3.1 \pm 0.57) \times 10^{-14}$</td>
<td>1000±0</td>
<td>620±28</td>
<td>$(8.2 \pm 0.28) \times 10^{-15}$</td>
</tr>
<tr>
<td>PP</td>
<td>0.027</td>
<td>$(12 \pm 2.8) \times 10^{-14}$</td>
<td>100±14</td>
<td>72±13</td>
<td>$(18 \pm 0.57) \times 10^{-14}$</td>
</tr>
</tbody>
</table>

*Errors were calculated by standard deviation of duplicate tests for each polymer.

The results of formaldehyde-PC desorption test under different temperatures collected by microbalance 1 are shown in Figure 4.11. Compared to desorption at 25 ºC, the desorption process at 40 ºC took much longer to reach equilibrium, suggesting that elevated temperature could retard the mass-transfer process. However, more formaldehyde was released from the PC film at higher temperature. In addition to temperature, the desorption process could be affected by $y$ during desorption and $C_0$ and. However, $C_0$ and $y$ for these two tests are summarized in Table 4.6, and show no significant difference.
**Figure 4.11** Comparison of desorption at different temperature

**Table 4.6** Parameters of desorption test under different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C₀ (g/m³)</th>
<th>y (g/m³) (sorption)</th>
<th>y (g/m³) (desorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>230</td>
<td>0.75</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>220</td>
<td>0.79</td>
<td>0</td>
</tr>
</tbody>
</table>

**4.4.2 Detection of formaldehyde polymerization on the film**

**4.4.2.1 Fluorimetry - PTFE tubing formaldehyde detection**

Fluorimetry tests results are summarized in Figure 4.12. As shown in Figure 4.12, neither the signal intensity of used tubing nor the signal intensity of fresh tubing show an increasing/decreasing tendency with time. On the contrary, the signal of both groups fluctuated within a narrow range during the testing, indicating there was no formaldehyde mass change in the reagent solution during the testing process. The fluctuation of both groups showed a consistent tendency, suggesting that the fluctuation might be caused by normal experimental noise. On the other hand, there was no obvious difference of emission signal intensity between two groups of samples. To qualify the difference between the results from each of the two groups, a two-tailed
paired t-test with a significance level of 0.05 was employed. The P-value of t-test was 0.16, which was more than 0.05, indicating there was no significance between signal intensity of two sample groups, and indicating that formaldehyde mass extracted from used PTFE tubing and new PTFE was not significantly difference. The signal intensity of used PTFE tubing was even slightly higher than that of fresh tubing, it might the caused by experimental error, or the interference of formaldehyde attached on the aluminum foil or on the glass bottle.

![Figure 4.12 Results of the first fluorimetry test for PTFE tubing](image)

In the second test, the sampling interval increased to 2.5 hours to allow formaldehyde to fully dissolve into the sulfuric acid solution. The test results are shown in Figure 4.13, the background signal intensity has already been deducted from the two groups. Only two data points were not sufficient to get a conclusion about the tendency of results. The P-value of two tailed paired t-test was 0.87, which was also much bigger than 0.05, showing that there was no statistic difference between two sets of data.

Fluorimetry test results indicate that there was no detectable formaldehyde sorbed onto PTFE tubing surfaces after exposure to formaldehyde. It also indirectly proved that there was no detectable short chain polyformaldehyde on the inner surface of PTFE tubing.
Figure 4.13 Results of the second fluorimetry test for PTFE tubing

4.4.2.2 Fluorimetry - PS formaldehyde detection

Figure 4.14 Results of fluorimetry test for PS film

The test results of fluorimetry testing of PS films is summarized in Figure 4.14. The expected formaldehyde mass in two disks cut from PS films after desorption test was 0.38μg and 0.21 μg.
while the expected formaldehyde mass in two disks cut from clean PS film was 0 μg. However, there was not an obvious difference between the measured formaldehyde mass extracted from clean and exposed films, as the measured formaldehyde mass extracted from all films was about 0.10 ~ 0.19 μg. The test results might be interfered by contaminants in air. Test results indicate that there was no formaldehyde or short chain formaldehyde soluted by sulfuric acid or reagent solution from PS films and failed to exclude the polyformaldehyde theory as formaldehyde left in the PS film might not exist as free monomers or short-chain polymer.

4.4.2.3 Aluminum foil sorption/desorption test

Figure 4.15 shows the mass change of aluminum foils during formaldehyde sorption testing collected by micro-balance 1. There was no obvious change of detected aluminum except for the second test for 0.0005 inch thickness aluminum foil. The results could be due to buoyancy caused by air flow, as the weight of thin aluminum films was smaller than the weight of the polymer films and could be easily affected by air flow. Compared to the thinner aluminum film, the thick film of higher weight with higher resistance to buoyancy effects, showed a relative constant rate of mass increase during testing.

![Figure 4.15 Formaldehyde-aluminum sorption test results](image)

When using the same mass change scale used for polymer substrates, the observable weight change
during sorption testing for each aluminum foil was negligible, as shown in Figure 4.16.

![Figure 4.16 Formaldehyde-aluminum sorption test results shown using a larger scale mass change scale](image)

Aluminum sorption tests results indicate there was no significant mass change during sorption, therefore there was no detectable formaldehyde polymer forming on the aluminum film surface. The results were consistent with the results of PTFE tubing fluorimetry tests.

The 0.002 inch thick aluminum film was taken from the balance, wrapped in aluminum foil, and stored in freezer at 0 °C for later FTIR analysis at NIST laboratories.

4.4.2.4 FTIR test results
Table 4.7 Details of films for FTIR analysis

<table>
<thead>
<tr>
<th>Film ID</th>
<th>Size (cm × cm)</th>
<th>Thickness (cm)</th>
<th>Expected formaldehyde mass in the film measured by micro-balance (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde-exposed PC film</td>
<td>5 × 5</td>
<td>0.0254</td>
<td>0.14</td>
</tr>
<tr>
<td>Fresh PC film</td>
<td>5 × 5</td>
<td>0.0254</td>
<td>0</td>
</tr>
<tr>
<td>Formaldehyde-exposed aluminum film</td>
<td>3.6 × 3.6</td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td>Fresh aluminum film</td>
<td>3.6 × 3.6</td>
<td>0.02</td>
<td>0</td>
</tr>
</tbody>
</table>

(a)

![Absorbance vs Wavenumber graph](image_url)

- Formaldehyde PC-down side1
- Formaldehyde PC-down side2
- Formaldehyde PC-up side1

Wavenumber values:
- 1098 cm⁻¹
- 936 cm⁻¹
- 900 cm⁻¹
The tests results from the FTIR surface analysis are shown in Figure 4.17, background sorbance spectrum values have already been deducted from results. The x-axis is wavenumber (cm\(^{-1}\)), which was the inverse of wavelength (cm). The y-axis is absorbance normalized on a scale of 0 to 1, where 0 indicates no absorption and 1 indicates complete absorption (Khan et al., 2012). As shown in Figure 4.17(a) and Figure 4.17(b), even though both PC film and aluminum films after formaldehyde exposure showed several peaks at different wavelengths, none of them related to polyformaldehyde or formaldehyde. In addition, surface analysis results of two sides of one aluminum foil were not identical, the distinction might be caused by difference characteristic of these two surface, as one surface was smoother than the other one. FTIR results are consistent with PTFE/fluorimetry test results there was no detectable polyformaldehyde or formaldehyde on the material surfaces. The indefinite peaks indicate that some unknown substance might form on the surface. It was also possible that the amount of polyformaldehyde was below the detection limit and failed to be detected by this technique. Another possibility is that polymerization of formaldehyde formed inside the films instead of on the surface.

4.5 Conclusions
In all sorption/desorption tests conducted at 0% humidity and 25 ºC, formaldehyde concentration in films reached steady state within 6~7 days during sorption. However, only a portion of formaldehyde sorbed to films was released during desorption. Thus the formaldehyde mass-
transfer process appears to be more complicated than for other VOCs. Diffusion maybe not be Fickian or some unknown reaction is interfering with mass-transfer reversibility. Formaldehyde desorption test at different temperatures suggested that increased temperature could retard formaldehyde diffusion rates in some polymer materials.

Fluorimetry testing of PTFE tubing found that there was no significant difference between new tubing and used tubing, indicating that there was no detectable formaldehyde on PTFE tubing surfaces. Aluminum sorption test also showed no significant mass change caused by formaldehyde during sorption. FTIR method analyzing films surface found no signal indicating the presence of polyformaldehyde. However, there was some slight difference between formaldehyde detected in exposed films and unexposed films, indicating some formaldehyde might exist in an unknown status on the films.

Diffusion of formaldehyde in selected polymers was irreversible and there was no detectable polyformaldehyde forming on the polymer surface at 25 °C, 0% RH. The irreversibility might be caused by formaldehyde detention in the film due to some unknown reaction or process. It was also possible that there was some polyformaldehyde formed inside the films instead of on the film surface.

4.6 References
ATSDR (2009) Public health statement, Division of toxicology and environmental medicine, Agency for Toxic Substances and Disease Registry, Division of toxicology and environmental medicine, GA.


amounts of formaldehyde in air with chromatomembrane cell and its sensitive determination by flow injection technique coupled with spectrophotometric and fluorometric detection. Talanta, 67(5), 1014-1022.


5. Conclusions

5.1 Summary
The study investigated formaldehyde mass-transfer properties using two distinctly different methods. First, formaldehyde sorption/desorption testing was conducted using several thin polymer films, PC, PS, PMMA, PE and PP. The formaldehyde mass-transfer properties parameters were determined by model fittings and calculations. Second, several analytical techniques such as fluorimetry and FTIR spectrometry were employed in an attempt to detect formaldehyde or formaldehyde polymer that might have formed on surfaces.

In all sorption/desorption tests conducted at 0% humidity and 25 °C, formaldehyde concentration in films reached sorption equilibrium within 6~7 days. However, only a portion of formaldehyde sorbed to films was released during a desorption cycle of the same duration. Thus the formaldehyde sorption process appears to be more complicated than other VOCs.

Fluorimetry testing of PTFE tubing showed no significant differences between new tubing and tubing that had been previously exposed to formaldehyde, indicating that there was no detectable formaldehyde on PTFE tubing surface. Aluminum foil sorption testing also showed no significant mass change resulting from formaldehyde exposure. FTIR analysis results found no (poly)formaldehyde on PC film surface or aluminum foil surface. However, indefinite peaks indicate that some unknown substance might present on the film and foil surfaces after exposure to formaldehyde.

5.2 Conclusions
Diffusion of formaldehyde in selected polymers was irreversible in all cases and there was no detectable polyformaldehyde forming on formaldehyde-exposed surfaces at 25 °C and 0% RH. The irreversibility might be caused by formaldehyde detention in the film due to chemical reaction or some unknown physical process. It was also possible that there was some polyformaldehyde formed inside the films instead of on the film surface.
Appendix

Sorption model

close all;
clear all;
T=300*2242; % calculation time (s)
time_step=300; % time step (s)
n=0; % indicates the current calculating time step
L=0.0127*0.01; % thickness of the film(m)
D=4.5*10^-14;
C0=2.267208*10^8; % initial concentration(ug/m3)
N=T/time_step+1; % number of calculation points
ratio=zeros(N,1); % M0/M
for time=0:time_step:T
    n=n+1
    i=0;
    sum=0;
    step_step=8/((2*i+1)^2*3.141592654^2)*exp(-1*D*(2*i+1)^2*3.141592654^2*time/L^2/4);
    sum=sum+step_step;
    while (abs(step_step)/sum>0.000001)
        i=i+1;
        step_step=8/((2*i+1)^2*3.141592654^2)*exp(-1*D*(2*i+1)^2*3.141592654^2*time/L^2/4);
        sum=sum+step_step;
    end
    ratio(n,1)=1-sum;
c(n,1)=ratio(n,1);
end

for i=1:1:(T/time_step+1)
xaxis(i)=300*(i-1);
induceddata=load('sorption.csv');
l=1;
sumgap=0;
for i=1:1:(T/time_step+1)
gap(l)=(induceddata(l,3)-ratio(l))^2;
sumgap=sumgap+gap(l);
l=l+1;
end %calculate the difference between model prediction and experimental data

plot(induceddata(:,1),induceddata(:,3), 'r', xaxis,c, 'b') %plot figures
ylabel('Formaldehyde concentration in chamber air (ug/m3)'); %set y-label
xlabel('Time (s)'); %set x-label
legend('Experimental data','Location','best', 'Model fit','Location','best') %set plot labels
title('Sorption model fit','FontName','Times New Roman','FontSize',16) %set title

Desorption model

close all;
clear all;
T=300*1176; % calculation time (s)
time_step=300; % time step (s)
n=0; % indicates the current calculating time step
L=0.0127*0.01; % thickness of the film(m)
D=14.5*10^-14;
C0=1.291259387*10^8; % initial concentration(ug/m3)
N=T/time_step+1; % number of calculation points
ratio=zeros(N,1); % M0/M
for time=0:time_step:T
    n=n+1
    i=0;
sum=0;
step_step=8/((2*i+1)^2*3.141592654^2)*exp(-
1*D*(2*i+1)^2*3.141592654^2*time/L^2/4);
sum=sum+step_step;
while (abs(step_step)/sum>0.000001)
i=i+1;
step_step=8/((2*i+1)^2*3.141592654^2)*exp(-
1*D*(2*i+1)^2*3.141592654^2*time/L^2/4);
sum=sum+step_step;
end
ratio(n,1)=sum;
c(n,1)=ratio(n,1);
end

for i=1:1:(T/time_step+1)
xaxis(i)=300*(i-1);
end

induceddata=load('desorption.csv');
l=1;
sumgap=0;
for i=1:1:(T/time_step+1)
gap(l)=(induceddata(l,3)-ratio(l))^2;
sumgap=sumgap+gap(l);
l=l+1;
end

%calculate the difference between model prediction and experimental data

plot(induceddata(:,1),induceddata(:,3), 'r', xaxis,c, 'b')       %plot figures
ylabel('Formaldehyde concentration in chamber air (ug/m3)');      %set y-label
xlabel('Time (s)');       %set x-label
legend('Experimental data','Lc
%set plot labels

%set title

title('Sorption model fit','FontName','Times New Roman','FontSize',16)

ation','best', 'Model fit','Location','best')