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A Literature Review on the Study of Moisture in Polymers

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ABSTRACT: This literature review covers the main chemical and physical interactions between moisture and the polymer matrix. Fickian versus Non-Fickian diffusion behaviors are discussed in approximating the characteristics of moisture sorption. Also, bound water and free water sorbed in polymers are distinguished. Methods to distinguish between bound and free water include differential scanning calorimetry, infrared spectroscopy, and time-domain nuclear magnetic resonance spectroscopy. The difference between moisture sorption and water sorption is considered, as well as the difficulties associated with preventing moisture sorption. Furthermore, specific examples of how moisture sorption influences polymers include natural fiber-polymer composites, starch-based biodegradable thermoplastics, and thermoset polyurethane and epoxies.

INTRODUCTION

Polymers are distinct from many materials, because at ambient temperatures, low molecular weight substances can freely migrate throughout the polymer structure. Therefore there is a desire to develop methods of preventing chemical and physical interactions with low molecular weight substances, such as gases and moisture.¹ Moisture and water sorption in polymers are particularly important to consider when optimizing drug formulations and electronics.^{2,3} In the case of drug formulations, it is crucial that the product remains chemically stable and performs consistently in a broad range of temperatures and ambient humidity levels once it reaches the consumer. Whereas polymers used in electronics, such as poly(methyl methacrylate) optical disk substrates, may bend or swell after moisture sorption following melt molding. In this case, problems often arise during production, prior to consumer interaction.³

The amount and rate of moisture absorption is dependent on temperature, relative humidity (RH) levels, as well the relative hydrophilicity of the polymer matrix, and the moisture sorption mechanism.⁴ One useful model to approximate the characteristics of moisture sorption is Fickian transport.

Equation 1. General diffusion law or Fick's second law of diffusion.⁴

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

Fickian transport is described by the general diffusion law, Equation 1. C is the moisture concentration (kg/m^3), t is the time (s), and D is the diffusion coefficient (m^2/s). The temperature dependence of moisture absorption is then described by Equation 2.

Equation 2. The Arrhenius equation.⁴

$$D = D_o \exp\left(-\frac{E_d}{kT}\right)$$

In Equation 2, D_o is a pre-factor, E_d is the activation energy, k is Boltzmann's constant and T is the absolute temperature. Equation 1 assumes that the diffusion coefficient is independent of moisture concentration. Additionally, Fickian diffusion does not account for polymer changes due to relaxation or degradation. Non-Fickian behavior explains such polymer relaxation processes and reactions between moisture and the polymer matrix, such as hydrogen bond formation.⁴ In general, if the moisture exposure time occurs before polymer relaxation takes place, only Fickian transport is considered. The length of time in which one may consider only Fickian diffusion is generally valid for less than ten days, dependent on the polymer and humidity levels.⁴ Whereas if moisture exposure time is long enough for the polymer to undergo relaxation, both Fickian and Non-Fickian transport must be taken into account. Note in Figure 1, the first 72 hours in which the sample is subjected to 60% relative humidity at 30°C are described by Fickian transport. The remaining time must then take Non-Fickian transport into account.

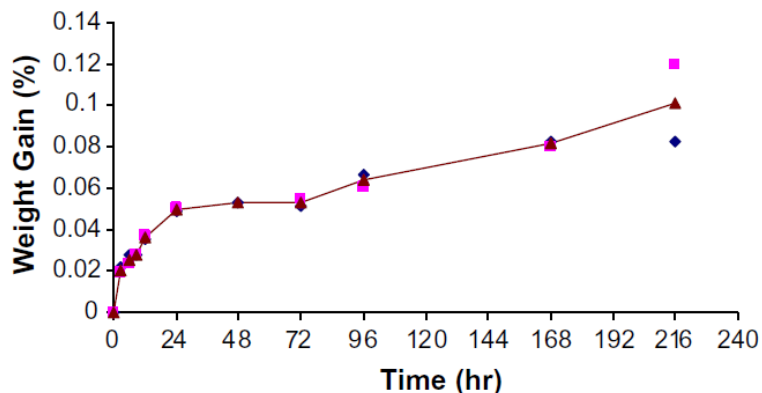


Figure 1. Moisture weight gain curve for a 0.6mm bismaleimide-triazine core sample subjected to 30°C/60% RH.⁴

Absorbed water effects every polymer differently, however there are generally two types of water found in polymers, free water and bound water. Free, or unbound, water does not come in direct contact with the solid polymer matrix. Free water in polymers exhibits the same transition temperature, enthalpy, and peak shape as pure water in differential scanning calorimetry (DSC).⁵ This phenomenon is shown in Figure 2. Peak I, denoting free water content, increases with increasing sorbed water in curve D. Additionally, free water molecules in solid polymers, denoted by peak 8 in Figure 3, reveal the same vibration modes as pure water in infrared (IR) spectroscopy.⁶ Bound water consists of water molecules which come into contact with the solid polymer. The water molecules act to break the intermolecular hydrogen bonds by forming hydrogen bonds with the hydroxyl groups of polymers.⁵ In hydrophobic polymers, water will even bind to the polymer by forming weak hydrogen bonds with atoms such as fluorine.³ In DSC, bound water has a lower transition temperature and a different peak shape than free water, as shown in Figure 2, where Peak II denotes bound water.⁵ Furthermore, the IR vibration mode for bound water, peak 7 in Figure 3, appears at a lower frequency than that of free water.⁶

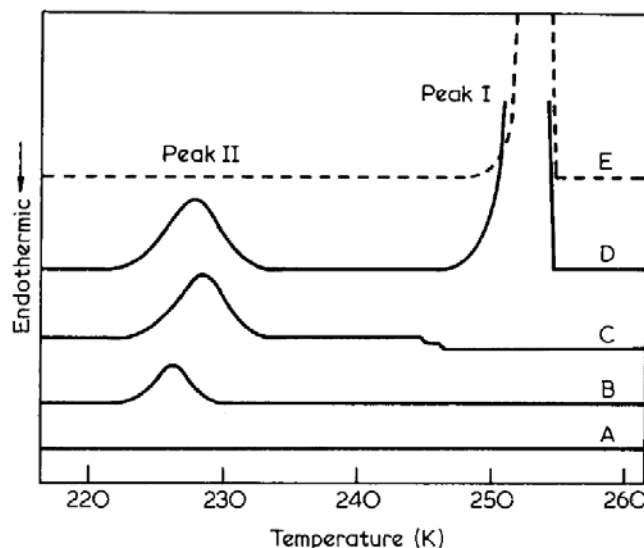


Figure 2. DSC cooling curves of water sorbed on poly(4-hydroxystyrene): the amount of sorbed water is 7.8% (curve A); 9.2% (curve B); 10.7% (curve C); 26.3% (curve D); and pure water (curve E). Peak I denotes free water and Peak II denotes bound water.⁵

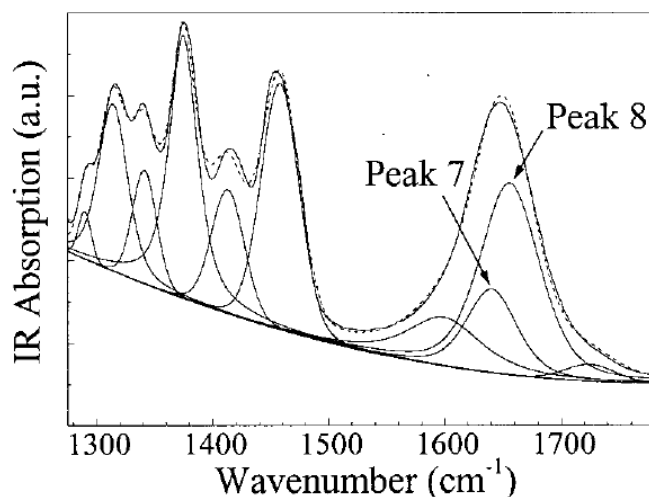


Figure 3. IR absorption spectrum of methylcellulose films at 90% RH. Peak 7 corresponds to bound water and peak 8 corresponds to free water, and the remaining peaks correspond to dry matter in the polymer film.⁶

CURRENT APPLICATIONS

As mentioned above, moisture content in polymers can be analyzed by differential scanning calorimetry and infrared spectroscopy. Other methods include thermogravimetric analysis, gravimetric studies, relaxation times in nuclear magnetic resonance spectroscopy, and dilatometric studies.⁵ Gravimetry, for example, was used in a 2009 study by Fan et al. to differentiate between water sorption and moisture sorption. Water sorption occurs when a polymer is immersed in water. Moisture sorption occurs when a polymer is in an environment with less than 100% relative humidity.⁴ In the study, Fan et al. measured the moisture weight gain for a

polymer coated with a hydrophobic membrane, and the same polymer with no coating. One set of coated and non-coated polymers was submerged in water at 60°C, while a second set was placed in a chamber with 60% RH at 60°C. The results shown in Table 1 reveal that moisture sorption and water sorption are different processes because the hydrophobic coating protects against water sorption, but has no effect on moisture sorption.⁴ Distinguishing between the water sorption and moisture sorption diffusion mechanisms requires further research.

Table 1. Effect of hydrophobic membrane on moisture sorption versus water sorption.⁴

Sorption condition	Hydrophobic film coated	Weight gain (%)
Water immersion (60 °C)	Yes	0.03
Water immersion (60 °C)	No	0.32
Moisture sorption (60 °C/60% RH)	Yes	0.31
Moisture sorption (60 °C/60% RH)	No	0.31

Natural fiber-polymer composites are another important focus for moisture sorption studies. Natural fibers, such as wood flour, jute, flax, and sisal, present an appealing way to reinforce polymers. This is due to their abundance, low cost, low density, high specific properties, and biodegradability.⁷ Unfortunately, natural fibers are prone to moisture sorption and must be processed at temperatures below 200°C to prevent thermal degradation.⁷ Also, the fibers naturally contain up to 20% moisture, and are largely influenced by relative humidity and temperature. This is a result of their hydrophilic structures with abundant hydroxyl groups available for hydrogen bonding with water molecules. Due to the hydrophilic fibers, reinforced copolymers such as wood flour-polypropylene are also very hydrophilic and moisture content increases with increasing fiber content.⁸ One impact that high moisture content has on the copolymers is generally an increased ability of the material and its structure to survive impact induced damages.⁸ This effect is reversible upon drying. Additionally, high moisture content in fibers can result in porous products.⁷ In an attempt to improve fiber processing techniques and control moisture content, chemical treatments and vinyl monomer grafting processes are being investigated and optimized. Ideally, the moisture content in natural fiber-polymer composites will eventually be sufficiently regulated for use in commercial products such as interior paneling in automobiles.⁷

Starch-based biodegradable plastics are also highly influenced by moisture content. Common examples are thermoplastics made with corn or potato starch.^{9,10} The starch is plasticized with varied amounts of water and glycerol and then processed as a thermoplastic. Studies by Shogren et al. and Soest et al. have determined that rates of aging increased with increased initial moisture content, particularly above 20% w/w. Starch-based thermoplastics are amorphous directly after processing. However, when initial moisture content is above 20% w/w, the thermoplastic becomes brittle as it ages due to a combination of water-loss via evaporation, structural changes, and free-volume relaxation processes. Water evaporation simply reduces the plasticizer content due to loss of free water. Yet, when initial water content is above 20% w/w, increased bound water content drops the glass transition temperature below room temperature. This allows the amorphous starch to crystallize at room temperature.⁹ The rate of crystallization increases as a function of water content. In addition, free-volume relaxation is a result of aging below the glass transition temperature and leads to an increased average relaxation time.⁹ Overall, the combined aging processes result in less flexible materials with higher tensile stress and elastic modulus.¹⁰ The most straightforward solution for increased aging at increased moisture content levels, would be to reduce the initial moisture content in the starch thermoplastics. However

controlling moisture content of extruded or molded products has not yet been optimized for industrial production processes.⁹

Thermoset polymers such as polyurethane and epoxy should also be considered when studying the effects of moisture in polymers. Polyurethane is hydrophilic and easily forms hydrogen bonds between the N–H and C=O groups of the polymer chains (Figure 4).¹¹ In polyurethane foams, water absorption increases with decreased foam density due to larger cell sizes and thinner cell walls. The thermal stability of polyurethane shape memory polymers and polyurethane foams is inversely related to water content due to the formation of thermally weak bonds such as biuret and allophanate with increased water content.¹²

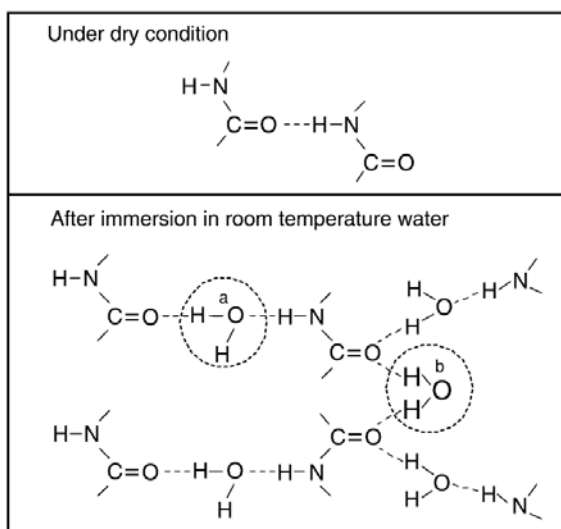


Figure 4. Effects of water on the hydrogen bonding of polyurethane shape memory polymer.¹¹

Bound water, pictured in the polyurethane shape memory polymer (Figure 4), reduces the glass transition temperature almost linearly as well as influencing the polymer's tensile behavior.¹¹ In contrast, free water in the polymer has negligible effects on either as it simply acts as a plasticizer. As described previously, differential scanning calorimetry may be used to determine the relative amounts of free and bound water in polymers such as polyurethane. Also, the free water is removed when the polymer is heated above 120°C, while the sample must be heated to 180°C to remove bound water.¹¹ Similar to polyurethanes, bound water in epoxies is a result of water molecules forming hydrogen bonds with the hydroxyl and amine groups in the thermoset polymer. In an epoxy, sorbed water acts as a crazing agent by decreasing mechanical strength with increased time spent in water. The concentration of polar groups in an epoxy or polyurethane may be measured indirectly by relating it to the equilibrium water sorption levels, which can in turn be related to the equilibrium glass transition temperature.¹

FUTURE DIRECTIONS

Currently, the most widespread methods of determining polymer water content and the ratio of bound and free water in polymers are differential scanning calorimetry and infrared spectroscopy.^{3,5,6} However an emerging method of determining both water content and the ratio of bound and free water in polymers is handheld, uniaxial, time-domain nuclear magnetic resonance spectroscopy. The method is a simple, rapid, and non-destructive. In addition, no sample

preparation is required.¹³ The instrument allows the user to differentiate between bound and free water because they each have distinct relaxation times.

In order to prevent chemical and physical interactions caused by water sorption, Fan et al. were successful in coating polymers in a hydrophobic membrane. However the same membrane had little to no success in preventing moisture sorption.⁴ Therefore future research should investigate the two sorption mechanisms and alternative methods to prevent both water and moisture sorption. Ideally the remedy would present a way to control initial moisture content as well; an important characteristic for materials such as natural-fiber composites and starch-based thermoplastics. Possible actions include coatings, chemical treatments, and grafting vinyl monomers onto surfaces to make the material more hydrophobic.⁷ This is imperative for hydrophilic polymers, specifically those used in drug formulations or electronics packaging, where chemical changes or swelling due to bound water are unacceptable. Until an effective method of preventing moisture sorption is developed, researchers should always consider the effects of moisture when optimizing polymers for a specific purpose.

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