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Structural and thermodynamic characterization of modified cellulose fiber-based materials and related interactions with water vapor

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ABSTRACT

In this study, the surface characteristics, water vapor interactions, and state of water adsorbed on unmodified and coated paper samples were investigated in an attempt to obtain a better understanding of the fundamental principles related to thermodynamics of this process, as well as to provide essential insight that could be used for further improvement of the papers' barrier properties. Based on the BET measurement, the coated paper samples showed higher specific surface areas than unmodified paper; however, their mean pore diameters are smaller. The BJH method was used for pore size distribution analysis. Hydrophobic properties of the paper samples were determined from experimental isotherms, e.g., monolayer moisture content, and these results have been related to the water vapor transfer rates (WVTRs) showing a complex nature of these relations. The highest peak corresponding to the modified samples with smaller pore sizes was found to be in the range of 1–30 nm, while it was in the 30–100 nm pore size range for unmodified paper. The net isosteric heats of sorption for different unmodified and modified paper samples were determined from water vapor adsorption isotherms measured at 15, 25, and 35 °C. The net isosteric heats of sorption decreased with an increase of moisture content after reaching the maximum values at 12.53, 15.25, 14.71, 23.2, and 22.77 kJ/mol for unmodified, zein grafted, calendered coated, PLA, and PHBV coated papers, respectively. The state of adsorbed water and water-vapor interaction on paper surface were also studied by TGA–DSC and FT-IR spectroscopic techniques. The FT-IR results revealed the formation of water vapor clusters due to poly-layer formation at the higher relative humidity. This has a profound effect on the equilibrium properties, e.g., the intensity of interactions between water molecules and the paper surface decreases as the relative humidity (moisture content) increases. Percentage of bound and unbound water formation and also the dehydration energy at various relative humidities were determined for the paper samples using the TGA–DSC technique.

1. Introduction

The non-biodegradable properties of synthetic polymers make them unsuitable for food or pharmaceutical packaging applications from an environmental point of view. A suitable way to overcome this problem is to replace them with biodegradable polymers, which can easily decompose when disposed as waste. Recently, cellulose fiber materials, like paper, have gained more attention for the application as packaging materials, since they are more environmentally friendly. However, cellulose fiber based materials are hygroscopic, easily adsorbing moisture when the relative humidity (RH) is high and losing it when the surrounding air is dry. Adsorbed water in the cellulose-based material affects the textural, technological qualities and long-term stability [1]. It also affects the water vapor transition rates (WVTRs) and permeabilities (WVPs) [2,3]. Moisture sensitive foods and pharmaceuticals should be placed in packaging with controlled water vapor and gas transmission rates to achieve the required quality, safety, and shelf life [4–6].

Hard and soft woods are reduced to cellulose fibers forming wood pulps for making paper products. The cellulose fiber possesses a high crystalline content, inaccessible to water molecules but also contains amorphous component to which water molecules can gain access. The main adsorption sites in cellulose fiber-based material are the hydroxyl groups, and also the carbonyl groups [7]. Adsorbed water molecule has a strong affinity for hydrogen bond formation with other polar polymers, like, cellulose fiber-based materials. Those that are closely associated with OH groups form monolayer water, but those not intimately associated with OH

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Table 1
Physical properties of paper samples.

Physical property	Paper types					
	Unmodified paper	Zein grafted/coated paper	PLA coated paper	PHBV coated paper	Commercial papers	
					Copy/printing (base-paper)	Calendered coated paper
Grammage (g/m^2)	60	88	115	110	85	150
Density (kg/m^3)	546	628	1153	967	850	1083
Thickness (mm)	0.11	0.14	0.13	0.12	0.10	0.14

groups form polylayer water [8]. The monolayer water molecules are non-freezing bound water because the motion of the water structures is strictly limited by the association with the surface [9,10].

Paper is a porous medium and has a macro-pore size in the range of 0.1–10 μm [11,12]. As the result of these, water vapor and gas penetrate easily through the paper. Porosity and pore size distribution in the paper affect its surface uniformity, moisture adsorption, homogenous ink uptake (printing ink) and so on [12,13]. Coating and filler materials reduce the pore size and pore volume to some extent as a result of blocking the pores between the fibers on the paper surface. There are a variety of physical techniques to measure geometry of pores on the material surface that include: gas adsorption isotherms, mercury intrusion porosimetry, solute exclusion, thermoporosimetry, nuclear magnetic resonance and microscopic techniques [12,14]. In this study, nitrogen and water vapor adsorption isotherms were used for the analysis of the specific surface area, pore sizes and pore size distribution for both unmodified and modified paper samples. Characterizing modified paper samples provides essential insight for a further improvement of the paper's barrier properties, in order to enhance its viability as a packaging material and quality paper.

The thermodynamics functions (total heat of sorption (Q_{st}), net isosteric heat of sorption (q_{st}), differential enthalpy (ΔH_d) and entropy (ΔS_d)), which can be obtained from sorption isotherms, provide useful information related to the binding strength between sorbed water vapor and adsorbent's surface, and energy requirements associated with sorption process [15–18]. Isosteric heat of water adsorption is a measure of energy that binds water molecules with substrate surface and, it is also identified with the energy required to remove moisture from material. Calorimetric techniques, e.g. differential scanning calorimetry (DSC) and thermogravimetry (TG) or combined simultaneous thermal analysis (STA), can also be applied to determine isosteric heat of water vapor on the materials [19–21].

Biopolymer films and/or coatings on cellulose fiber materials have the potential to increase the water vapor barrier properties. Biodegradable materials, such as polylactic acid or polylactide (PLA), poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), and zein have shown a significant potential as packaging materials. These bio-based polymers have also been used for modification of cellulose fiber materials in order to enhance water barrier (mass transfer) properties and reduce hygroscopicity. It is therefore important to understand the physical and chemical treatments applied to paper surface and how they affect the surface characteristic, e.g., interaction between water and modified cellulose. In our earlier study we have reported transport (barrier) properties of the paper samples that were also used in this study [2,3]. This study focuses on structural and thermodynamics properties of the samples to better understand the physical and chemical treatments applied to paper surface and how they affect the surface characteristics, through measuring pore sizes, adsorption isotherms and analyzing interaction between water molecules and modified cellulose surface. The main objectives of this study can be summarized as follows:

- To examine the specific surface area, pore size and pore volume of modified paper samples and compare to unmodified paper sample (reference sample).
- To determine equilibrium properties of different paper samples, e.g., monolayer water contents, from experimental isotherms and relate these properties to WVTRs.
- To determine the net isosteric heats of sorption (q_{st}) from water vapor adsorption isotherms and the formation of adsorbed water and its energy of interaction on the modified paper surface at different relative humidity levels using FT-IR and TGA–DSC spectroscopic techniques.
- To use the results obtained above in order to get better understanding of water vapor transfer properties in different papers.

2. Materials and experimental

2.1. Preparation of samples

Several types of paper samples that were prepared for this study are listed in Table 1. Unmodified paper sample was made from pure cellulose pulp. Modified paper samples, such as PLA and PHBV coated paper, with coating weight of 25–30 g/m^2 on the base paper (85 ± 4 g/m^2), as well as zein grafted paper (∼28 g/m^2 zein coating weight) were prepared according to procedures further explained in this section. The PLA was purchased from NatureWorks, LLC; PHBV, with a hydroxyvalerate content of 3 wt.% was purchased from Sunrise Global, Inc., NJ, USA and chloroform used as the solvent was purchased from Sigma–Aldrich (Shanghai) Trading Co. Ltd. All compounds were used without further purification. PHBV and PLA coated paper were prepared through solution bar coater machine by dissolving 0.306 g powder of each sample in 6 ml of chloroform at 50 °C afterward sonicated for 1 h [22]. Each coating solution was then spread onto printing paper surface (10 cm × 10 cm, thickness 90 μm) mounted on a Teflon sheet using a glass bar coater machine at room temperature and dried under ambient conditions (23 ± 2 °C) for 24 h.

Zein, a class of prolamine protein-based natural products with highly hydrophobic and barrier properties, was grafted onto the paper sheet (60 g/m^2) consisting of sulphite fiber using Isophorone Diisocyanate (IPDI) as a coupling agent. The zein solution was prepared by dissolving a certain amount of zein powder in the mixture of 70% acetone and 30% water (v/v) [23]. Then the additive-free hand sheets were reacted with the diluted zein solution and the IPDI at the temperature of 50–60 °C, followed by a magnetic stirring for a few hours. The samples were finally washed several times and oven dried overnight at 100 °C before the characterization tests were carried out.