

Kinetics and Equilibria of Water Sorption in LLDPE-Cellulose Composites

INTRODUCTION

The sorption of water by nonpolar polymers containing a filler depends mainly on the nature of the filler. For hydrophilic fillers such as cellulosic fibers, an increase in water sorption may be expected. Cellulose has unique water sorption properties. It initially shrinks on absorption (up to about 3–4%) and then swells with increasing water content. This results in the development of shear stresses along matrix-filler interfaces leading to delamination and debonding. Ultimately, water in a composite material affects such properties as dielectric loss, electrical resistance, and mechanical strength. Our concern is with the growing interest in cellulose-containing polyolefine compounds. These require exposure to relatively high temperatures, typical of processing such polymers. The question therefore arises whether the water sorption properties of such composites conform to expectations based on principles as, for example, the rule of mixtures. The present brief communication shows that water sorption is a complex phenomenon that requires detailed study.

EXPERIMENTAL

Materials and Preparation of Composites: Linear low density polyethylene (LLDPE) and Whatman CF-1 chromatographic grade fibrous cellulose powder were used. The LLDPE was a commercial grade having a melt flow index of 1.5, and was supplied by Dow Chemical Co. The arithmetic average fiber length in the Whatman powder is about 200 μm as determined from a Kajaani FS-100 fiber classification instrument. Samples containing 0–40% cellulose were prepared on a Brabender mill ($T = 160 \pm 2.5^\circ\text{C}$), compression-molded at $T = 158^\circ\text{C}$ and then quenched rapidly in cold water. All samples were kept under high vacuum (10^{-5} Torr) for a 2-week period to remove residual water. Samples were weighed at regular intervals until no further weight loss was detected. Failure to follow this procedure could result in appreciable scatter in water content values.

Determination of Water Content: Following immersion in distilled water (23°C or boiling water), the 0.5 g samples were wiped with filter paper to remove surface water and weighed to ± 0.00001 g. Water content, per unit mass of cellulose, was calculated by way of the parameter \mathcal{L} defined as

$$\mathcal{L} = (m_w - m_d)(C_F + 1)/(m_d C_F) \quad (1)$$

where C_F is defined as the ratio of weight parts of cellulose to weight parts of polymer and m_d and m_w are the masses of dry and wet samples, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the equilibrium water content of composites on their cellulose content, as expressed by $C_F/(C_F + 1)$ [see eq. (1)]. A linear increase with cellulose content is evident. The equilibrium moisture content is independent of the immersion temperature, but it does depend on preparation conditions, for example, mixing for short times (e.g., < 5 min) produces samples with higher sorptive properties. Results to be published separately show that treatment of cellulosic fibers with stearic acid or silane coupling agent also does not significantly affect the overall equilibrium water content.

The kinetics of water sorption are shown in Figure 2 where the normalized concentration of water m/m_f (where m = amount of water content at any given time; m_f = equilibrium water content) is plotted against the square root of time. At room temperature (curves A and B), the rate of water sorption is very low; however, it increases rapidly with temperature (curve C). A comparison of A and B shows that the rate of water sorption is only slightly dependent on cellulose content: The sample containing less cellulose reached equilibrium more rapidly. The

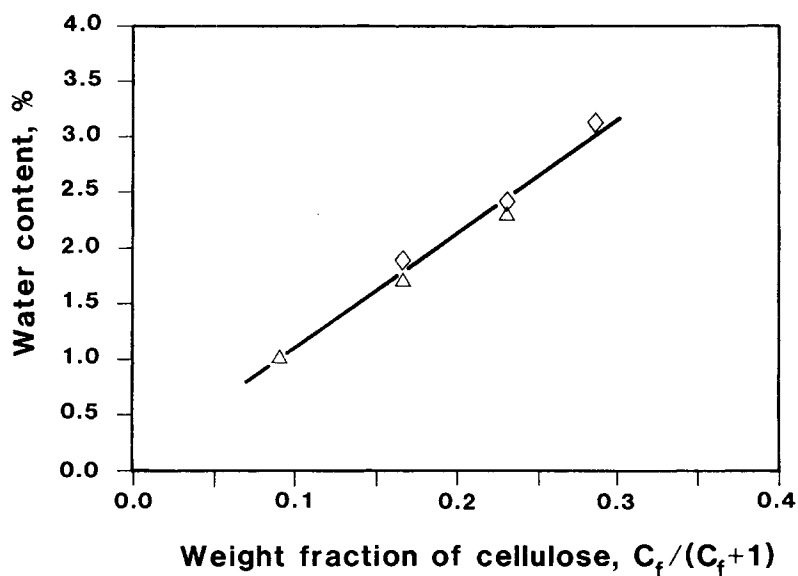


Fig. 1. The dependence of equilibrium water content in composites on cellulose content. Immersion temperature ($^{\circ}\text{C}$): (Δ) 23; (\diamond) 100.

intercept point indicates a very rapid initial sorption of water. This could be due to the uptake of water by exposed cellulosic fibers located at the surface of the composite. The presence of such fibers has been confirmed by the use of a water-based Herzberg stain.

The main issue considered in this communication is the equilibrium water content of PE-based composites. The data in Figure 1 and the use of eq. (1) show that, over the range of cellulose content studied, the cellulose itself takes up 11% water. This is significantly lower than the equilibrium water content of free cotton cellulose which has earlier been reported as 22%¹ but is now believed to be closer to 50%.² Assuming for present purposes that polyethylene is a

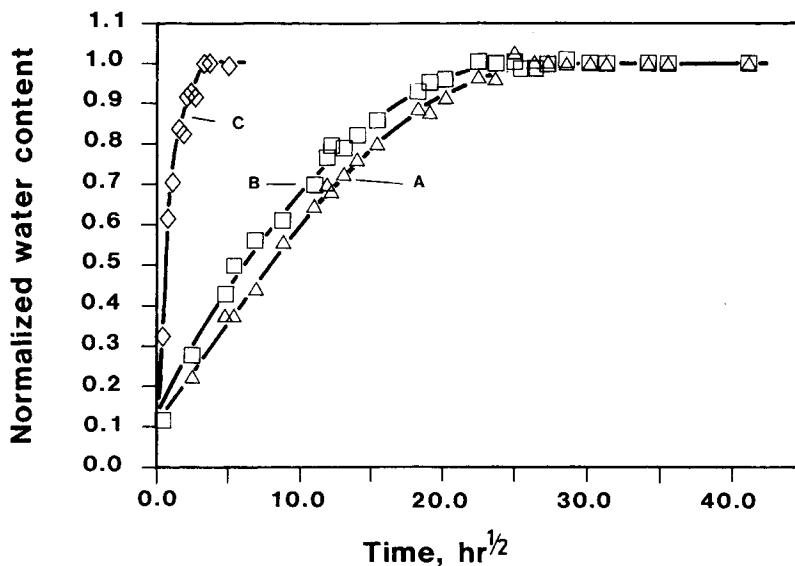


Fig. 2. Kinetics of water sorption in LLDPE-cellulose composites. Immersion temperature ($^{\circ}\text{C}$): (A and B) 23; (C) 100. Cellulose content (%): (\square) 10; (\diamond) 20; (Δ) 30.

hydrophobic matrix and that little adhesion occurs at the interface between the matrix and the hydrophilic fiber, the above result presents an anomaly. Expectations arising from the rule of mixtures, which should be applicable in a case such as this, would place the equilibrium water content near that of the cellulose alone.^{3,4}

The lower than expected water sorption may result from such causes as a reduced degree of mobility of water within the polyethylene matrix, from mechanical restrictions due to the swelling of fibers, or from a modification of the cellulosic fiber as a result of high-temperature processing. In this respect Sefain and Shukry⁵ have found that thermally treated cotton linters show a significant decrease in water retention. According to these authors, structural changes in cotton cellulose take place upon exposure to high temperatures. For example, cotton cellulose treated at 160°C for 30 min reduces its moisture retention value by roughly one-half. Similarly, the water take-up rates are decreased after thermal treatment.⁶

In contrast, however, recent studies by Klason et al.⁷ report that, after boiling, the moisture content in HDPE-cellulose flour composites is in the range 7–10 wt%. This corresponds to about 30% moisture per unit weight of cellulose, a value which is close to that fiber's equilibrium (saturation) value.

Evidently the question of thermally induced morphological changes in cellulose is not resolved. Our data, however, strongly support the findings of Sefain and Shukry,⁵ raising the possibility that the structural changes alluded to are critically associated with a temperature in the 160–200°C interval. Exposure time also appears to be an important variable, since a higher water level was observed for samples mixed for short times (< 5 min). Among the practical consequences of this study is the possibility that the water sensitivity of cellulose containing composites may be controllable within certain limits by thermal pretreatment of the cellulose component. This treatment could also be designed into a processing regime for the composite. Further research is needed to identify the true causes for the effects reported here and in the literature. Pertinent, detailed studies are underway in our laboratories.

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