Carbohydrate Research 361 (2012) 120–126

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Influence of glycerol on molecular mobility and hydrogen bond network in amorphous glucose matrix

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ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form 24 August 2012
Accepted 25 August 2012
Available online 4 September 2012

Keywords:
Glucose
Glycerol
Molecular mobility
Hydrogen bond network
Phosphorescence

ABSTRACT

The effect of glycerol on molecular mobility and hydrogen bonding in amorphous glucose matrix was studied. Phosphorescence from erythrosin B (Ery B) was used to characterize the temperature dependence of mobility in glucose/glycerol films over the temperature range from 100 °C down to −10 °C. Analysis of emission energy and excited state decay kinetics from Ery B provided information about thermally activated modes of matrix dipolar relaxation around and collisions with the excited triplet state of the probe. Both the average rate of matrix mobility and the width of the distribution of matrix mobility rates largely scaled with the effect of glycerol on the glass transition temperature of the glucose/glycerol mixture. The IR hydrogen bond bandwidth increased at higher glycerol content, suggesting that the strength of the bond became more widely distributed with the added glycerol. An increase with temperature in the hydrogen bond peak frequency indicated the transformation of associated hydroxyl to free hydroxyl. These results support a model in which glycerol plasticizes the glucose matrix at mole ratios of 0.1 and above while providing no evidence for the antiplasticization seen in other sugar matrices.

1. Introduction

Glucose, one of the most widely distributed and important sugars in nature, possesses considerable application value for the food and pharmaceutical industries. It is used in abundance as a food additive, filler, and as a component in tablet coatings. As an amorphous (noncrystalline) solid, glucose can also act as an effective protectant against lipid oxidation and bacterial growth.[1] The stability and properties of amorphous biomaterials are modulated by specific physical processes and chemical reactions that are directly modulated by the molecular mobility of the amorphous matrix.[2] Thus, it is of primary importance to understand the molecular mobility of amorphous solids containing glucose and its response to changes in composition and environmental conditions. Experimental techniques such as NMR, DSC, and fluorescence have been extensively used to evaluate the mobility of amorphous biomaterials;[3–7] we have systemically used phosphorescence of Erythrosin B (Ery B), a triplet state molecular probe, to monitor the molecular properties of protein and oligosaccharide matrices.[8–11]

Glycerol is widely used as a humectant and cryoprotectant as well as a softener or texture modifier to improve the properties and stability of many foods and pharmaceutical preparations. Small molecules such as glycerol and water can enhance the flexibility and ductility of polymeric materials, an effect termed plasticization.[12–14] The effects of those small molecules on the physical properties of amorphous solids have also been studied. It has been reported that glycerol can exert different effects depending on its concentration. In sucrose, for example, the extent of matrix relaxation and the rate of non-radiative quenching due to matrix collisions monitored using Ery B phosphorescence decreased at temperatures below the matrix T_g when the ratio of glycerol/sucrose (mole/mole) was lower than 0.27, indicating that glycerol was acting as an antiplasticizer at low concentrations.[15] Different concentration-dependent effects of glycerol were also found in other amorphous solids. Lourdin et al. reported that glycerol at a content below 12% could increase the ductility of potato starch film; when the amount of glycerol exceeded 12%, however, the ductility decreased.[16] Similar antiplasticizing effects of glycerol were also found in the matrices of trehalose and maltodextrin.[17,18] In most cases, there exists a critical content that marks the onset of a change in functionality from antiplasticizer to plasticizer.

The role of glycerol in films is determined by its effect on at least two types of molecule motions in matrix: large-scale molecular motions (α-relaxations) and localized molecular motions (β-relaxations). The molecular mobility at any temperature relative to the glass transition is greatly influenced by molecular weight of the compound forming the matrix. Previously we have reported that matrix molecular mobility varies in the order glucose < maltose < maltotriose in the region from 40 °C below to 40 °C above the glass-transition temperature, indicating that the molecular mobility is actually higher in sugars with compounds with higher molecular weight.[19–21] The hydrogen bond network is an important

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0008-6215/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carres.2012.08.013

factor modulating those molecular motions in amorphous solids. The number, length, and strength of hydrogen bonds within the matrix will inevitably affect interactions between the molecules in the matrix, consequently affecting the molecular mobility. FTIR, an effective chemical analysis method, is widely used to detect the status of hydrogen bonds in amorphous carbohydrate glasses.[22–24] The sugar OH stretching frequency detected by FTIR provides a sensitive indicator of the strength of the hydrogen bonding network. In this study, the temperature dependence of stretching frequency was measured to quantify how the strength of hydrogen bonds is modulated by matrix composition.

Although there have been extensive studies about the effect of glycerol on polymeric materials,[25–27] the effects of glycerol on glucose, a simple but extremely important sugar, have not yet been reported. This study thus assessed the effects of glycerol on the mobility of amorphous glucose using phosphorescence from the triplet probe erythrosin B (Ery B) dispersed in the matrix. Glycerol content was varied from 0 to 0.4 (mole ratio of glycerol/glucose) by adding glycerol to the glucose solution before film formation. The temperature-dependence of mobility was measured and analyzed at different glycerol contents, generating families of mobility versus temperature curves. Samples under the same conditions were measured by FTIR in a temperature range from 30 to 100 °C. By studying the relation of mobility to hydrogen bond strength and network, we can better understand the mechanism of glucose mobility in the amorphous solid state.

2. Results and discussion

2.1. T_g of glucose–glycerol matrix

As a plasticizer, glycerol is added to change the properties of a material, primarily through depression of the glass transition temperature (T_g). The T_g values for amorphous dry glucose/glycerol binary mixtures calculated from the Couchman and Karasz equation were 38 °C, 30 °C, 23 °C, 17 °C, and 11 °C for mole ratios of 0.0, 0.1, 0.2, 0.3, and 0.4, respectively. The thickness of the glucose films used in this study was <1 mm. Previous experience indicates that seven days is sufficient time to equilibrate such amorphous sugar samples with a dry environment; water content in a pure sucrose film made by this method was negligible (0.56 ± 0.13 wt.%) and increased to about 4.5 wt.% in sucrose/glycerol films with high glycerol content after extensive drying.[15] In order to ensure removal of residual water, the films were thus flushed with dry N_2 at 100 °C at the beginning of each experiment.[2]

2.2. Delayed emission spectra

The delayed emission spectra of Ery B in amorphous glucose/glycerol films displayed two bands: a longer wavelength phosphorescence band (maximum ~690 nm) due to emission from the lowest triplet state (T_1) and a shorter wavelength delayed fluorescence band (maximum ~555 nm) due to emission from the first excited singlet state (S_1) repopulated by thermally stimulated reverse intersystem crossing from T_1. Delayed emission spectra of Ery B in glucose with varying glycerol content collected over the temperature range from −10 to 100 °C showed a decrease in phosphorescence (I_P) and increase in delayed fluorescence (I_{DF}) intensity with increasing temperature as expected for this probe (data not shown). Both the delayed fluorescence and phosphorescence bands shifted to longer wavelength at higher temperature. The intensity ratio of delayed fluorescence to phosphorescence was analyzed as a van't Hoff plot of $\ln(I_{DF}/I_P)$ versus $1/T$ (Fig. 1) and the linear slope was used to calculate the energy gap (ΔE_{TS}) between the T_1 and S_1 states. Van't Hoff plots were linear with R^2 ⩾0.995. The slopes of samples containing varying contents of glycerol showed negligible differences, indicating that ΔE_{TS} was not affected by addition of glycerol.

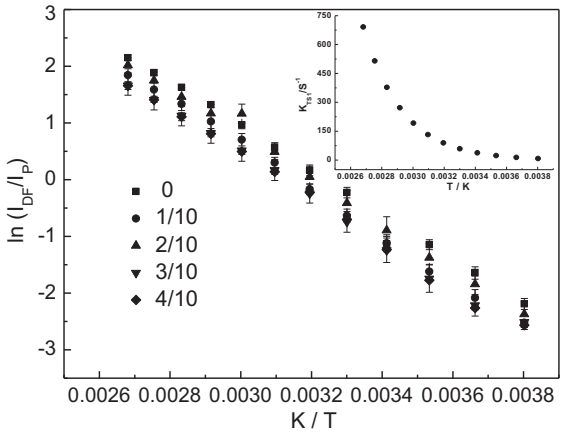

Figure 1. Natural log of ratio of peak intensity for delayed fluorescence (I_{DF}) to phosphorescence (I_P) ($\ln(I_{DF}/I_P)$) for Ery B in glucose films containing varying mole ratios of glycerol plotted versus inverse temperature. Insert shows the values for $k_{TS1}(T)$ in these films calculated as described in the text.

Delayed fluorescence emission from Ery B occurs because the rate or reverse intersystem crossing (k_{TS1}) is comparable to or faster than the rate of emission (k_{RP}). As outlined in Materials and methods (Section 4.3), k_{TS1} is the product of a base rate ($k°_{TS1}$) and an Arrhenius factor and is thus temperature-dependent. As reported in the literature, $k°_{TS1}$ for Ery B varies with matrix composition from $0.3 \times 10^7\ s^{-1}$ in ethanol and $6.5 \times 10^7\ s^{-1}$ in water[28] to $111 \times 10^7\ s^{-1}$ in solid polyvinyl alcohol.[29] We estimated the maximum possible value for $k°_{TS1}$ in glucose/glycerol by assuming that the values of $k_{TS1}(T)$ calculated using (Eq. 5) cannot result in values for k_{TS0} (calculated from lifetimes using (Eq. 4)) that decrease with temperature;[29] the values obtained are thus the minimum possible values of $k_{TS0}(T)$. The value of $k°_{TS1}$ determined from such analysis and used for this study was $3 \times 10^7\ s^{-1}$; the insert in Figure 1 shows the values of $k_{TS1}(T)$ calculated over the temperature range from −10 to 100 °C.

The peak frequency (ν_P) and bandwidth (Γ) for phosphorescence emission, determined by fitting emission spectra to a log-normal line shape function (Eqs. 2 and 3), are plotted in Figures 2 and 3, respectively, as a function of T–T_g to emphasize their dependence on the physical state of the films. The peak frequency was approx-

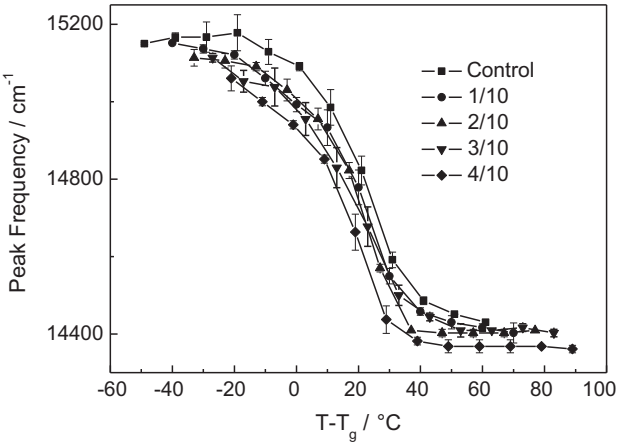

Figure 2. Temperature dependence of the peak frequency for phosphorescence emission from Ery B in amorphous glucose/glycerol films.