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Research Article

Molecular Mobility in Mixtures of Absorbed Water and Solid Poly(vinylpyrrolidone)

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Poly(vinylpyrrolidone) (PVP) was used as model system to examine molecular mobility in mixtures of absorbed water with solid amorphous polymers. Water vapor absorption isotherms were determined, along with diffusion and proton NMR relaxation measurements of absorbed water. Concurrently, measurements of glass transition temperatures (T_g) and carbon-13 NMR relaxation times for PVP were determined as a function of water content. Two water contents were used as reference points: W_m, obtained from the fit of water absorption isotherms to the BET equation, corresponding to the first shoulder in the sigmoid isotherm; and W_g, the amount of water necessary to depress T_g to the isotherm temperature. Translational diffusion coefficients of water, along with proton T_1 relaxation time constants, show that both the translational and the rotational mobility of the water is hindered by the presence of the solid polymer and that the absorbed water is most likely represented by two or more populations of water with different modes or time scales of motion. The presence of "tightly bound" or immobilized water at levels corresponding to W_m, however, is unlikely, since water molecules maintain a high degree of mobility, even at the lowest levels of water. Above W_g, water shows an increase in mobility with increasing water content, but it is always less mobile than bulk water. With increasing water content, carbon-13 T_1 relaxation time constants for PVP, measured under the same conditions as above, indicate a major increase in the molecular mobility of carbon atoms associated with the pyrrolidone side chains.

KEY WORDS: molecular mobility; water; poly(vinylpyrrolidone); nuclear magnetic resonance; diffusion; relaxation.

INTRODUCTION

This study is concerned with the behavior of solid systems consisting of mixtures of amorphous polymers and residual water. Such mixtures occur with polymers used as pharmaceutical excipients after exposure to water during processing or to high relative humidity. Such amorphous solids include celluloses, starches, synthetic hydrogels, and proteins. Previous work has shown that the uptake of water as a function of relative humidity and temperature occurs by means of absorption into the amorphous regions of the polymer and that this process of dissolution is generally exothermic, leading to a decrease in absorption with increasing temperature (1–3). More recent studies have shown that when water is absorbed into such amorphous solids, it acts as a placticizer, causing an increase in free volume and a reduction in the glass transition temperature (T_g) (4,5). The enhanced molecular mobility caused by the plasticization of such solid systems was recently proposed to be the major underlying factor in the effects of water on the chemical and physical instability of amorphous pharmaceutical solids (6).

In a recent study of the amorphous polymer, poly(vinylpyrrolidone) (PVP), water absorption isotherms obtained over the range of −40 to 60°C were analyzed in conjunction with measurements of T_g as a function of water content (1,5). From these data it was possible to obtain W_g, the amount of absorbed water that reduces the value of T_g to the operating temperature, T. Thus, for water contents below W_g, the polymer/water mixture was in the highly viscous glassy state, while above W_g the system was transformed to the rubbery state, with a greatly increased molecular mobility. It was shown that W_g corresponds to the point on the isotherm where the amount of absorbed water increases significantly. This was also found to be the region of the isotherm where water is believed to take on "solvent-like" properties and where water induces significant physical and chemical change.

Using the BET equation (7) or equations related to it (8) to fit the absorption isotherms, it also is possible to determine the constant, W_m. For vapor adsorption onto solid surfaces this constant is equal to the weight of adsorbed vapor required to form a complete monolayer on the solid surface. Although the use of such an equation has no theoretical basis for water absorption into amorphous solids, the value of W_m obtained for such systems has been shown to have some

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physical significance. The excipients microcrystalline cellulose and compressible sugar, for example, lose their direct compaction properties at water contents just below W_m (9), and gelatin capsules become brittle as the water content is reduced below W_m (10). It has been suggested that below W_m, water molecules are in a "tightly bound" or "highly immobilized" state and, thus, not available to act with solvent-like characteristics (11). In the recent study of PVP at various temperatures (1,5), however, it was found that W_m and W_g changed with temperature in a very parallel manner. This led to the suggestion that perhaps both W_m and W_g are related to water contents at which significant physical changes in the polymer occur due to plasticization by water and that a "tightly bound" state of water is not necessary to explain such behavior.

In the present study, the role of water in affecting the properties of a model amorphous solid, PVP, has been probed further. The molecular mobilities of both the absorbed water and the polymer as a function of water content have been directly and concurrently examined through measurements of rotational and translational motion using nuclear magnetic resonance spectroscopy (NMR) and gravimetric techniques. The specific objective of this study is the quantitation of the extent of molecular mobility change for water and the polymer as water content passes through regions described by W_m and W_g.

MATERIALS AND METHODS

Materials

Poly(vinylpyrrolidone) (PVP K-90) was obtained from the General Aniline and Film Corporation (Wayne, NJ). The average molecular weight, determined from intrinsic viscosity measurements, was 360,000, which agreed with the manufacturer's listed value. Gel permeation chromatography showed a very broad molecular weight distribution. Since previous studies with PVP K-30 (with an average molecular weight of 90,000) showed no difference in the water absorption behavior of dialyzed versus untreated PVP (1), no further purification treatment was performed.

All salts employed as saturated solutions for relative pressure control were used as received from the suppliers. Lithium bromide, potassium acetate, copper(II) chloride, ammonium chloride, and lithium sulfate were obtained from Aldrich Chemical Co. (Milwaukee, WI). Sodium hydroxide, magnesium chloride, potassium carbonate, magnesium nitrate, sodium bromide, potassium iodide, sodium chloride, potassium chloride, and potassium nitrate were obtained from Mallinckrodt, Inc. (Paris, KY). Lithium chloride and potassium dichromate were obtained from J. T. Baker, Inc. (Phillipsburg, NJ). Calcium bromide and potassium bromide were obtained from E. M. Science (Cherry Hill, NJ).

The glass vials used in the pulsed field gradient NMR experiments were autosample vials, part No. 801, obtained from Sun Brokers, Inc. (Wilmington, NC). The deuterated benzene and deuterated chloroform used as lock solvents in the proton NMR studies were obtained from Aldrich Chemical Co. (Milwaukee, WI). The solvents contain 0.1% (v/v) tetramethylsilane (TMS) as a reference compound. The 5.0- and 2.5-mm-outer diameter NMR tubes used in the proton NMR studies were obtained from Wilmad Glass Company, Inc. (Buena, NJ). The 9.5-mm Kel-F rotors used in the solid-state NMR experiments were obtained from Chemagnetics Inc. (Fort Collins, CO).

Determination of Water Vapor Absorption Isotherms

A series of Pyrex glass or Nalgene desiccators was prepared with saturated salt solutions providing various relative pressures (12). Approximately 0.5 g of PVP K-90 samples were placed in glass scintillation vials, dried at 105°C under vacuum for 12 hr, and weighed prior to placement in the desiccators. The samples were weighed weekly and assumed to be at equilibrium when the sample weight change from the previous measurement was no more than 5 mg/g. The experiments were performed in triplicate.

Measurement of Glass Transition Temperature

Differential scanning calorimetry (DSC) was performed on PVP K-90 samples equilibrated at various water contents using a Perkin-Elmer DSC-7 instrument equipped with a thermal analysis data station (Perkin–Elmer Corp., Norwalk, CT). Helium was used as a purge gas. The heated block of the instrument was cooled using a liquid nitrogen reservoir. Temperatures were calibrated by reference to transition temperatures of both indium (156.64°C) and mercury (−38.86°C). Enthalpy calibration was performed in reference to indium. A heating rate of 20°C/min was found to be optimal for observing and recording transitions in PVP. Sample weights ranged from 5 to 15 mg. The samples were sealed in coated aluminum pans (Dupont Instrument Co., Wilmington, DE) to prevent moisture loss during measurements. The first run with each sample typically showed an endotherm at T_g, due to physical aging, that did not appear in subsequent runs. The reported values of T_g are the onset values from the second DSC run.

Determination of Translational Diffusion Coefficient of Water by the Absorption/Desorption Gravimetric Technique

Free films of PVP (200 mm in thickness) were prepared by casting an ethanolic solution of PVP K-90 onto coated paper (Warren Release Paper, ultracast patent, S. D. Warren Co., Chicago, IL) using a spin casting technique. The cast film was dried in a vacuum desiccator over phosphorous pentoxide for at least 24 hr, then vacuum-dried for 24 hr at 110°C. Film thickness was determined using a micrometer (series, 70, No. M-1001, J. T. Slocomb Co., Glastonbury, CT). The film was cut into rectangles using a No. 11 scalpel blade and the dimensions were determined using a magnifying reticle (Edmund 6× graphic arts comparator, Edmund Scientific Co., Barrington, NJ).

Diffusion coefficients were determined at 25°C by the interval absorption/desorption gravimetric method (13) using an electrobalance vacuum assembly described previously (12). A PVP film sample of known thickness was placed in the vacuum assembly, thermostated at 25°C, dried under vacuum, and exposed to an environment of constant relative vapor pressure. The weight gain due to absorption of water vapor was monitored as a function of time on a chart recorder. The results were plotted according to

$$\frac{M_t}{M_\infty} = 4(Dt/\pi l^2)^{0.5} \quad (1)$$

where M_t is the amount of diffusant taken up at time t, M_∞ is the equilibrium uptake attained theoretically after infinite time, l is the thickness of the film, and D is the diffusion coefficient. The diffusion coefficient was determined from the initial slope of a plot of M_t/M_∞ versus $(t/l^2)^{0.5}$, which was linear up to a value of about 50% of M_t/M_∞. Since the diffusion coefficient is concentration dependent, both sorption ($\overline{D}_s$) and desorption ($\overline{D}_d$) experiments were performed and the mean $\overline{D}$ was then calculated as $\overline{D} = \frac{1}{2}(\overline{D}_s + \overline{D}_d)$. Above a weight fraction of water of 0.15, the initial slope of the data was not linear when plotted according to Eq. (1), due to deformation of the film during water absorption. Therefore, the diffusion coefficient of water could not be determined above this water level using this technique.

Determination of Translational Diffusion Coefficient of Water by the Pulsed Field Gradient Spin Echo Technique

The diffusion coefficients of absorbed water were examined in three samples of PVP powder containing weight fractions of water of 0.19, 0.28, and 0.31. Samples at lower water contents (less than a weight fraction of 0.19) did not yield a signal (spin echo) and could not be studied by this technique. The samples equilibrated at the highest relative vapor pressures, containing water greater than a weight fraction of 0.31, were too sticky to be accurately transferred, and therefore, the diffusion coefficients could not be determined at these water contents.

The diffusion coefficients were determined on a Chemagnetics CMC-300A (300-MHz) spectrometer (Chemagnetics Inc., Fort Collins, CO) using a pulsed field gradient spin echo nuclear magnetic resonance spectroscopy technique (14). A modified Chemagnetics solenoid probe capable of operating at the proton frequency (300 MHz) was used. The probe had been modified to accommodate the gradient coil and to allow implementation of the pulsed field gradient experiment (15). The pulsed field gradient was supplied by a quadrupole gradient coil with a field gradient strength of 52 G/cm amp. The construction, calibration, and operation of this instrument for the pulsed field gradient experiment were described previously (15). Tuning of the probe, tuning of the 90° pulse width, and shimming were performed on a reference sample of pure water. Temperature control at 25°C was provided by forcing air through the variable temperature coil. A Chemagnetics RKC REX C1000 temperature controller was used to regulate the temperature. The diffusion coefficients were determined by performing a series of pulsed field gradient experiments in which the duration of the gradient pulses, δ, was varied and the echo time, τ, and field gradient strength, G, were fixed at 16.6 msec and 102 G/cm, respectively. The echo amplitudes were determined by baseline-correcting the resulting time domain signals and taking the maximum in the time domain signal as the echo amplitude. Diffusion coefficient was then calculated by performing a weighted nonlinear least-squares regression of the echo amplitudes to Eq. (2):

$$A(2 \cdot \tau) = A(0)\exp\left[-(\gamma G\delta)^2 D\left(\Delta - \frac{\delta}{3}\right)\right] \quad (2)$$

A is the echo amplitude, γ is the gyromagnetic ratio, and Δ is the gradient pulse interval.

NMR Determination of Proton T_1 of Absorbed Water

Each sample for the proton NMR studies was placed in a capillary NMR tube, sealed, and coaxially placed in a 5-mm NMR tube containing a deuterated lock solvent. In this manner, the intrinsic mobility of the material contained in the inner capillary tube was not affected by the lock solvent. PVP K-90 samples were attached to the vacuum electrobalance assembly described previously (12), dried, and equilibrated at various water contents with vapors of various saturated salt solutions. The equilibrated samples were then sealed in the tube, which ensured that the water content of the sample was constant during the proton NMR measurements. Since the water contents in the sealed tubes could not be directly determined, the water contents of these samples were taken to be the same as values obtained from the desiccator studies. For comparison purposes, samples of pure water were also prepared, as well as solutions of PVP K-90 representing weight fractions of water equal to 0.80, 0.85, 0.90, 0.95, and 0.98.

Proton NMR spectra were recorded at 300 MHz on a Bruker high-resolution multinuclear Fourier transform NMR spectrometer (Bruker Instruments, Inc., Billerica, MA). The proton T_1 measurements for the resonance signals of water in the above samples were performed using an inversion-recovery pulse sequence. Typical 90 and 180° pulse widths were 12.1 and 24.2 msec, respectively. A list of 16 values of the variable delay, τ, was used and 16 acquisitions were performed. Delay times were set to be greater than five times the anticipated T_1. The T_1 values were calculated from the nonlinear fit to Eq. (3):

$$M_Z = M_0\left[1 - 2\exp\left(\frac{-\tau}{T_1}\right)\right] \quad (3)$$

where M_z, the magnetization in the z direction, is determined from the signal intensity after the 90° pulse and M_0 was determined from the maximum value of the signal intensity that can be obtained at very long tau values.

Since the T_1 relaxation of protons in aqueous heterogeneous systems is often complicated by cross relaxation, or magnetization transfer, between the water protons and the protons present in the substrate, it was necessary to determine if cross relaxation was a factor in the relaxation behavior of the water in the PVP systems. The method of Grad and co-workers (16) was used to test for cross relaxation.

Determination of Carbon-13 T_1 by Solid-State CP/MAS NMR

The poly(vinylpyrrolidone (PVP K-90) samples were equilibrated at various relative water vapor pressures yielding water contents up to a weight fraction of water of 0.28 and then tightly packed into 9.5-mm Kel F rotors. Higher weight fractions of water could not be examined using this technique due to problems with spinning the viscous samples. The carbon-13 solid-state cross polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance spectra were obtained using a Chemagnetics M-200 solid-state spec-

trometer operating at resonance frequencies of 200 and 50 MHz for proton and carbon-13 nuclei, respectively. A spinning rate of 3.2 kHz was used. The chemical shifts were externally referenced using the hexamethylbenzene peak at 17.36 ppm.

A cross polarization inversion recovery pulse sequence was used to determine T_1 (17). The optimum contact time for cross polarization was found to be 1 msec. The 90° pulse widths ranged from 5.1 to 5.6 msec for proton and 7.2 to 8.5 msec for carbon-13. A delay time of 4 sec was used between successive sampling pulses. The typical spectral width was 10 kHz. Each T_1 experiment accumulated 100 to 200 scans. A series of eight tau values was tested in triplicate. The values for the carbon-13 T_1 relaxation time constants were calculated using linear regression analysis from

$$M_{net} = 2M_{cp}(0)\exp\left(\frac{-\tau}{T_1}\right) \quad (4)$$

where M_{net} is the magnetization after the last pulse in the sequence, M_{cp} (0) is the initial value of the magnetization, and τ is the delay time between pulses. An external temperature controller, consisting of a heat exchanger that was placed in a small dewar of liquid nitrogen or dry ice/isopropanol mixture, was used to perform measurements at temperatures below ambient.

RESULTS AND DISCUSSION

Water Vapor Absorption and Effects on Glass Transition Temperature

Figure 1 depicts the water vapor absorption isotherm for PVP K-90 at 25°C in units of weight fraction of water. Measurements of water vapor absorption isotherms for PVP K-90 at 4, 25, and 60°C (data not shown) yielded excellent agreement with isotherms obtained at these temperatures for PVP K-30, indicating no differences in the amount of water absorbed per unit mass of PVP (5).

Figure 2 depicts a plot of T_g for PVP K-90 as a function of water content. The T_g decreases significantly as water vapor is absorbed, in excellent agreement with results reported earlier for PVP K-30 (5). Also shown in Fig. 2 is the good fit of these data to the Fox equation, a simple mixing rule:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (5)$$

where T_g is the observed glass transition temperature, W_1 is the weight fraction of water, W_2 is the weight fraction of the polymer, T_{g1} is the glass transition temperature of the water, and T_{g2} is the T_g of the polymer (18). The glass transition temperature of water was assumed to be −137°C (19).

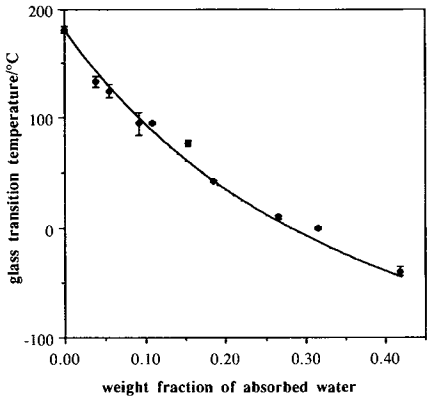

Fig. 2. Glass transition temperature of PVP K-90 as a function of water content. The line represents the fit to the Fox equation (see text) and the error bars represent the standard deviation.

Translational Diffusion Coefficients of Water

In Fig. 3, the diffusion coefficients of absorbed water in PVP are plotted over the whole range of water contents studied. Also shown in Fig. 3 are the two "critical regions" W_m and W_g described above. The three points representing the highest water contents were obtained using the pulsed field gradient technique, while the lower values were calculated from sorption–desorption data. The highest water content studied by the absorption/desorption measurement and the lowest water content studied by the NMR technique gave similar results indicating a general consistency in results between techniques.

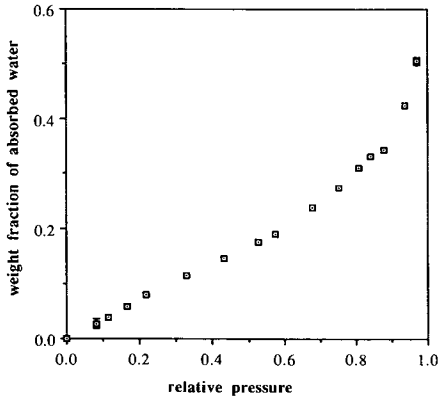

Fig. 1. Water vapor absorption isotherm for PVP K-90 at 25°C. Error bars represent the standard deviation.

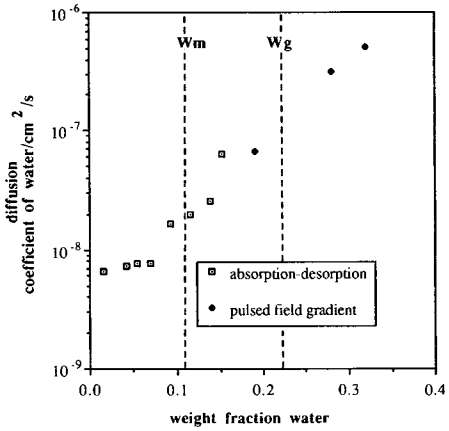

Fig. 3. Translational diffusion coefficients of water in PVP at 25°C as a function of water content.

Results from the pulsed field gradient spin echo technique showed a slight deviation from linearity at the higher values of the timing parameters when plotted according to Eq. (2). Such deviations have been reported in the literature for water in biological systems (20) and have been attributed to the presence of more than one population of water. This result indicated that the motion of the water could not be represented exactly by a single mode or time scale of motion and that more than one population of water may be contributing to the results. A simple calculation was performed on these data assuming that the diffusion coefficient was a weighted average of two diffusion coefficients for two populations of water, and the second population was found to represent a very small fraction of the total, less than 0.1%. Thus, the effective diffusion coefficients determined from the linear portion of the curves are reasonable estimates of the major mode of translational diffusion of water.

As shown in Fig. 3 the diffusion coefficient decreases exponentially as the water content is decreased, as has also been reported for starch/water systems (21). Most importantly, there is no critical change at W_m or W_g. Clearly, the motional freedom of the water molecules becomes more restricted as water content is decreased, being reduced about two orders of magnitude. However, the value of the diffusion coefficient at a weight fraction of water of 0.015, the lowest water content examined, is equal to 6.5×10^{-9} cm^2/sec, which clearly indicates that the water molecules still possess a high degree of translational mobility and are not "tightly bound" or "immobilized" in the glassy polymer structure. To illustrate this more clearly, a simple calculation using the Einstein equation for simple diffusion,

$$x = \sqrt{2Dt} \tag{6}$$

illustrates that it would take only 0.76 sec for a water molecule to diffuse a macroscopic distance of 1 mm at the lowest water content studied, indicating that the water is indeed quite mobile. It is also important to note that the diffusion coefficients of water at the highest water levels studied, in excess of W_g, are more than one order of magnitude less than that expected for the free diffusion of bulk water. Thus, water molecules in the absorbed state are somewhat restricted by the polymeric structure, even at higher water contents. Finally, from these results it is also important to recognize that the diffusion coefficient of absorbed water in PVP does not appear to be sensitive to the significant increase in free volume at the glass transition region of the polymer.

NMR Relaxation Studies

Typical proton NMR spectra at 25°C and 300 MHz for the PVP samples equilibrated at various water contents are shown in Fig. 4. Spectra for pure water, a PVP solution, and dry PVP are also shown for reference purposes. The proton peaks present at 0.00 and 7.14 ppm are due to TMS and residual protons in the deuterated benzene lock solvent, respectively. There are some proton peaks present from 0.00 to 2.00 ppm, possibly due to PVP protons or to minor impurities present in the PVP itself. The pure water shows a sharp proton resonance at 4.75 ppm. Since the dry PVP has no peaks present in this region and since the presence of

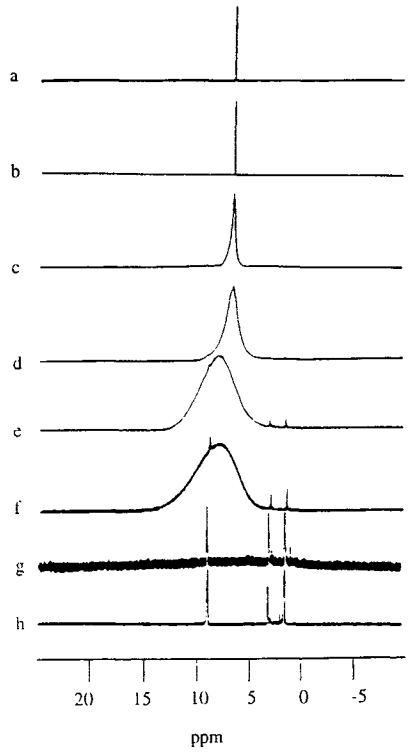

Fig. 4. Proton NMR spectra of different weight fractions of water in PVP K-90 at 300 MHz. Spectra for pure water, a PVP solution, and dry PVP are also shown for reference purposes. Numbers represent weight fraction of water: (a) 1 (pure water); (b) 0.850 (PVP solution); (c) 0.50; (d) 0.334; (e) 0.275; (f) 0.176; (g) 0.266; (h) 0 (dry PVP).

cross relaxation between the protons of the polymer and the protons of PVP was ruled out using the method of Grad and co-workers (16), the broad proton peaks at approximately 4.75 ppm in the samples equilibrated with water can be attributed to the absorbed water protons only.

The PVP samples containing low amounts of water had very broad proton peaks in the region of the water resonance. At higher water levels, the line widths decreased, indicating an increase in water mobility at higher amounts of absorbed water. At the highest levels of absorbed water, the peaks did not have Lorentzian or Gaussian line shapes (as expected for liquids and solids, respectively) (22) but were abnormally shaped. These abnormalities in the line shapes may have resulted from sample inhomogeneity at higher water contents where the sample had been significantly plasticized. At the highest levels of absorbed water, the line width of the water resonance was much broader than that of pure water or water in PVP solutions, indicating that the absorbed water never attains the mobility of pure water, even at the highest water levels. This observation is consistent with the differences observed in values of translational diffusion of water in the absorbed versus free state described above.

Proton T_1 relaxation time constants were determined using the inversion-recovery method described above. All data for liquid systems gave a good fit to Eq. (3), with the value of T_1 for pure water at 3.28 sec being in good agreement with the reported literature value of 3.6 sec (23). The data for systems containing absorbed water did not fit the single exponential relaxation described by Eq. (3) as did the

liquid systems, particularly at the lower water contents. Many other studies in the literature have found that the relaxation of water in the presence of a solid polymeric material does not follow a single exponential (24–26). Since the presence of cross relaxation with the protons of PVP was ruled out, such a poor fit may have resulted from the presence of two (or more) populations of water, each with a different relaxation process (25). In many studies, the poor fit to a single exponential relaxation has been ignored and a computer fit has been used to determine a single effective T_1, T_{1eff} (26). Others have fit the data to a two (25)- or three-state model (24). In the present case where some biexponential relaxation appeared to occur, one of the relaxation times clearly predominated. Therefore, it was still possible to obtain a single effective T_1, representing an average for all possible populations of water, by nonlinear regression analysis using Eq. (3). The effect of water content on the water proton T_{1eff} is illustrated for a single temperature, 25°C, in Fig. 5, along with the values representing W_m and W_g. This plot includes T_1 relaxation time constants determined for aqueous solutions of PVP, representing the highest water contents, and T_{1eff} values for absorbed water in solid PVP, representing the lower water contents. Unfortunately, this technique could not be used to determine the proton T_1 values below water contents associated with W_m, since the raw data did not fit Eq. (3) in any manner. Most likely, a greater proportion of water molecules is becoming associated directly with PVP at W_m through hydrogen bonding, thus giving rise to a greater proportion of molecules in more than one absorbed state and, hence, more than one relaxation time constant.

The T_{1eff} values shown in Fig. 5 initially decrease with increasing absorbed water, go through a minimum, and finally increase, approaching (but never reaching) the T_1 value for pure water. Such behavior has also been reported for the proton T_1 of water in regenerated cellulose (27). Like the results from the translational diffusion studies for water vapor, it appears that the proton T_1 values change in a continuous manner throughout the whole range of water contents examined, indicating that the mobility is changing with no discontinuities at W_g. These results also indicate that the absorbed water is not as mobile as pure water.

In Fig. 6, the water proton T_{1eff} relaxation time constants are plotted as a function of temperature for four water contents. The T_g of the PVP at each water level is illustrated by the dashed lines. These plots show that temperature appears to have a similar effect to water content, where the T_{1eff} is initially decreased by an increase in temperature, goes through a minimum, then increases. The presence of a minimum in T_{1eff} is much more apparent in these plots, especially at the higher water contents examined (see Discussion). Again, there is no correlation between the change in T_1 and the location of T_g.

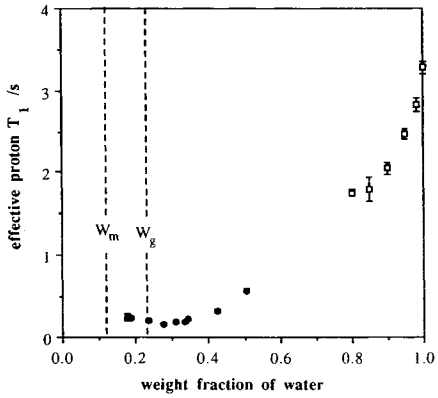

Fig. 5. Effective proton T_1 of water in PVP at 25°C. Error bars represent the standard deviation. (●) Absorbed water in solid PVP; (□) water in PVP solution.

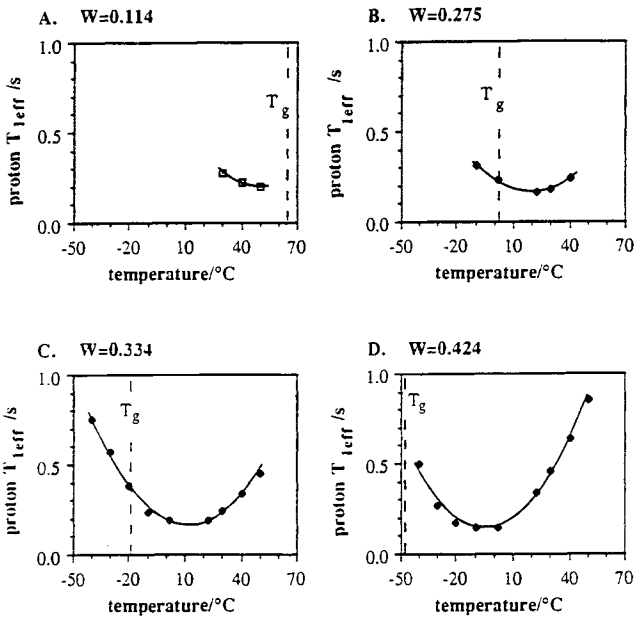

Fig. 6. Effective proton T_1 of absorbed water in PVP at four water contents as a function of temperature. The curves drawn through the data points do not represent a fit to any model and are drawn only to illustrate trends.

The finding that the changes in the water mobility are not related to changes in T_g is supported by a recent study examining the rotational mobility of probes in PVP as a function of water content using electron spin resonance (28). In this study it was found that water had a large effect on T_g but no correlation was found between T_g and the mobility of the solute probes. This result can be explained by the difference in time scales used to determine the water mobility and the T_g of the polymer, since NMR (as well as electron spin resonance) probe much faster modes of motion than the methods used to determine glass transition temperatures (such as differential scanning calorimetry).

To relate such T_1 relaxation time constants to mobility, the concept of a correlation time is often used. The correlation time, τ_c, is the average time for rotational or translational motion of a molecule. T_1 relaxation is related to molecular mobility, since such motion can cause fluctuating magnetic fields with which the nuclear spin system can interact to undergo relaxation back to the equilibration state. To relate T_1 to correlation time, a model must be invoked. Often, the simple model of Bloembergen, Purcell, and Pound (BPP) is used (29). In this model it is assumed that two identical spins are relaxing through isotropic, random, intramolecular rotational motion described by a single corre-

lation time and that the molecule is represented by a rigid sphere in a viscous continuum. According to this model, as the correlation time decreases or the molecular mobility increases, T_1 values will decrease, go through a minimum, and increase. The presence of the minimum depends on the frequency of observation.

Therefore, the presence of the minimum in the T_1 of the absorbed water in PVP is consistent with the basic aspects of the BPP theory, indicating that the molecular mobility is increasing with both water content and temperature. Unfortunately, the data do not quantitatively fit the simple BPP model, and therefore correlation times cannot be calculated. This probably results from the fact that the BPP model is too simplistic to describe the actual water mobility and that two or more correlation times are most likely necessary to describe the dynamics of the system. However, from the position of the minimum the correlation times for absorbed water can be estimated to be of the order of 10^{-9} to 10^{-10} sec, indicating that the water is not as mobile as pure water, with an approximate correlation time of 10^{-12} sec.

Carbon-13 Solid-State NMR Relaxation Studies of PVP

Figure 7 shows a typical solid-state carbon-13 NMR spectrum of PVP obtained using cross polarization and magic angle spinning at a field strength of 50 MHz. The peak designations of the four carbon resonances are from the literature (30). The peak at 19 ppm represents the C-2 carbon on the pyrrolidone side chain, while the peaks at 32 and 43 ppm each result from the superposition of two carbons which cannot be resolved in the solid-state spectrum. The T_1 relaxation time constants were determined for these three carbon resonances at 19, 33, and 43 ppm. The carbonyl peak at 170 ppm was not monitored quantitatively because such

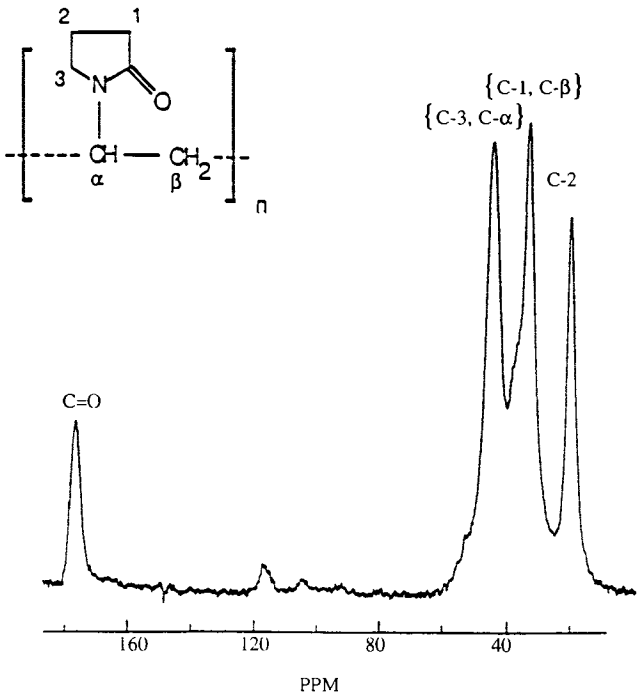

Fig. 7. Solid-state CP/MAS carbon-13 NMR spectrum of PVP K-90 at 50 MHz.

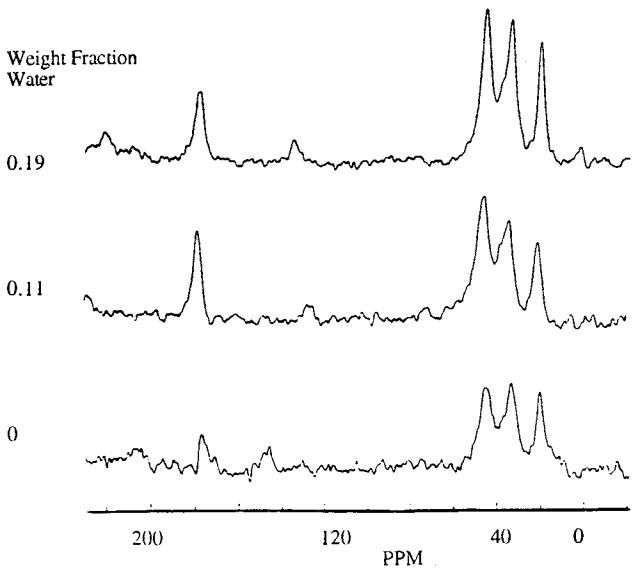

Fig. 8. Effect of absorbed water on the solid-state CPMAS carbon-13 NMR spectrum of PVP K-90 at 50 MHz.

carbons with no bonded protons have extremely large T_1 values. This would have required experimental time periods for accumulating data that would have been too long for the conditions under which such experiments could be conducted.

Figure 8 shows a series of PVP solid-state carbon-13 NMR spectra at several water contents. The carbon resonances are sharpest at the highest water contents and become more broad as the water content is decreased, the carbonyl peak being the most affected. It is uncertain at this point if the peak broadening results from a decrease in polymer mobility at the lower water contents, since it may also result if the optimal cross polarization time differs at the various water contents.

The T_1 relaxation time constants of the first three carbon resonances as a function of water content in PVP at 2°C are plotted in Fig. 9, along with values of W_m and W_g at 2°C. The carbon-13 T_1 values are highest in the dry PVP for all three peaks and decrease with increasing water content until a weight fraction of water of 0.15 is reached. At this water level the carbon-13 T_1 values appear either to level off or to go through a broad minimum. More data at higher weight fractions of water would be necessary to determine the actual presence of a minimum. Such data, however, are very difficult to collect with PVP owing to problems associated with spinning the rubbery, plasticized samples at the higher water contents.

The primary advantage of using carbon-13 NMR relaxation as a probe of molecular mobility is that specific functional groups can be studied. Thus, the general plasticizing effects of the water can be related to specific chemical portions of the polymer. All of the carbons on PVP undergo a significant change in molecular mobility as water is added, as reflected by the change in T_1 illustrated in Fig. 9. It is of particular interest to note that the carbon uniquely associated with the pyrrolidone side chain, C-2, is significantly affected by water. Attention is being focused on this carbon because it is the one carbon that yields a single peak in the

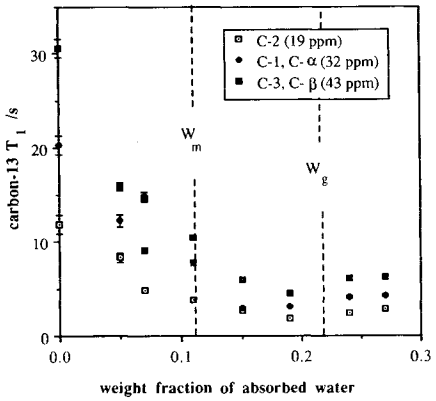

Fig. 9. Carbon-13 T_1 relaxation time constants of three PVP resonances as a function of water content at 2°C and 50 MHz.

solid state spectrum, and because the extent of contribution from the backbone carbons to the changing T_1 values and molecular mobility at these low water contents around W_m cannot be assessed from this work. The decrease in the carbon-13 T_1 of this C-2 carbon as a function of water content, therefore, is clearly indicative of an increase in the mobility or a change in the mode of motion of the polymer side chain. It is interesting that the greatest change in the T_1 values with increasing water content occurs below a water content of W_m.

Rather than calculating correlation time constants from carbon-13 T_1 data, the effect of temperature on the T_1 values is often used to elicit information on polymer mobility. The T_1 relaxation time constants of the three carbon resonances, however, were found to be insensitive to temperature over the temperature range examined (− 30 to 20°C) for two levels of water (data not shown). This may be indicative of a very low activation energy associated with these modes of molecular motion, or it may be due to the fact that the T_1 values were going through a minimum in the temperature range examined. Further examination of these temperature effects would be necessary to elucidate the nature of the changing mobility fully.

CONCLUSIONS

In this study the water vapor absorption isotherms for poly(vinylpyrrolidone), PVP, and the change in its glass transition temperature, T_g, as a function of water content, were determined. From these data, W_g, the amount of absorbed water required to reduce the T_g of PVP to any operating temperature. T, and W_m, the BET constant, were estimated. Both amounts of water appear to be in critical regions of water content where water has significant effects on the properties of amorphous solids.

The molecular mobilities of both water and PVP have been measured as a function of water content to examine the extent of mobility change and, in particular, whether or not changes in molecular mobility were sensitive to any critical changes in polymer structure taking place at W_m or W_g. For water, translational diffusion coefficients and T_1 relaxation time constants (reflective of rotational motion) show that marked increases in mobility occur as water is increased. However, the mobility of the water molecule on both time scales does not show any sensitivity to the transformation of the polymer from a glassy state to a rubbery state, presumably because of its small molecular size relative to the free volume of the polymer matrix. It is clear from both measurements that water molecules absorbed in PVP are neither "tightly bound" at low water contents nor absolutely "free" at the higher water contents. From both the NMR diffusion measurements and the T_1 relaxation studies, it appears that as the water content decreases, at least two populations of water molecules might exist, with different time scales or modes of motion. At lower water contents, the water may be associated directly with PVP and has a limited mobility, while beyond W_m the more mobile population of water is assumed to predominate.

Preliminary carbon-13 NMR T_1 measurements of PVP as a function of water content indicate that water, even below a value of W_m, has a profound effect on the molecular mobility of PVP. By focusing on the peaks of specific carbons it was possible to show that the increased mobility due to water was associated with the motion of the PVP side chain. It is not as clear whether or not backbone mobility is also affected.

It is concluded from these studies that in evaluating the role of water on the solid-state properties of amorphous polymers, more consideration should be given to the state of polymer and less to the extent to which water is bound or unbound in these samples. This study has clearly shown that significant rotational and translational mobility exists for water, even at very low water contents, and that the effect of water content on the mobility of the amorphous solid is the more critical factor.

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