The Water Vapor Sorption Behavior of a Galactomannan Cellulose Nanocomposite Film Analyzed Using Parallel Exponential Kinetics and the Kelvin-Voigt Viscoelastic Model

Barbara A. Keating,[1] Callum A. S. Hill,[2] Dongyang Sun,[2] Rob English,[2] Phil Davies,[3] Charles McCue[3]

[1]Department of Mechanical and Aerospace Engineering, The University of Strathclyde, Glasgow G1 1XJ, United Kingdom
[2]Forest Products Research Institute, Joint Research Institute for Civil and Environmental Engineering, Edinburgh Napier University, Edinburgh EH10 5DT, United Kingdom
[3]Waters, Atlas Park, Simonsway, Manchester M22 5PP, United Kingdom
Correspondence to: B. Keating (E-mail: barbara.keating@strath.ac.uk)

ABSTRACT: Nanocomposite films have been developed where a galactomannan (guar) matrix was reinforced with cellulose nanowhiskers and plasticized using sorbitol. The properties of these films were compared with films made from guar only. The films were examined using scanning electron microscopy and dynamic vapor sorption. The sorption kinetics properties were analyzed using parallel exponential kinetics (PEK) and this data interpreted using the Kelvin-Voigt (K-V) viscoelastic model. Substantial differences in sorption behavior were noted between the guar and cellulose reinforced guar films. Addition of cellulose nanowhiskers (CNWs) to the guar resulted in a change in the shape of the isotherm, as well as a reduced equilibrium moisture content throughout the hygroscopic range. With the guar film, hysteresis between the adsorption and desorption branches of the isotherm occurred up to 75% RH, where it collapsed. Dynamic mechanical analysis showed that the collapse of the hysteresis loop occurred at the glass transition temperature of the guar film. However, addition of CNWs to the guar produced a film where sorption hysteresis was found to occur throughout the hygroscopic range. The applicability of the K-V interpretation of the sorption kinetics is discussed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2352–2359, 2013

INTRODUCTION

Cellulose is an abundant, natural, renewable and biodegradable biopolymer which occurs in a wide variety of living species. Its structure is that of a linear polymer of D-anhydroglucose units joined by β-1, 4-glycosidic linkages. Cellulose fibers can be natural or man-made and the crystal structures are designated cellulose I, II, III, and IV.[1] Cellulose I has two polymorphs: I_α and I_β.[2–5] Cellulose microfibrils are considered to be comprised of crystalline and amorphous regions. Crystalline segments can be extracted in the form of nanowhiskers using sulfuric acid hydrolysis to etch away the "amorphous" regions.[2,6–8] These cellulose nanowhiskers (CNWs) are rod shaped particles with varying dimensions and aspect ratio that depends on the cellulose source. They form stable aqueous colloidal suspensions due to the presence of negative charges on their surfaces.[2,9] The Young's modulus of CNWs has been determined by both experimental[4,10–16] and simulation methods[14,17,18] to be ~140GPa. CNWs have been extensively studied for use as reinforcing

elements in composite materials. Reviews concerning cellulosic nanocomposites include those of Eichhorn[2] et al.,[3,19] Samir et al.,[20] Hubbe et al.,[21] and Dufresne.[22]

Polysaccharides can potentially be used as natural matrices in composite applications and investigations into the use of various polysaccharides for this purpose have been conducted at the Forest Products Research Institute over several years. In one such study, galactoglucomannans were found to exhibit interesting gelling behavior with CNWs and were subsequently selected for further study. Galactomannans consist of a mannose backbone with galactose side groups. Guar gum is a galactoglucomannan originating from the seed endosperm of the guar plant, *Cyamopsis tetragonolobus*, an annual plant that grows mainly in the semiarid regions of India. The ratio of mannose to galactose in guar gum is around 2 : 1. The principal backbone is a chain of (1–4)-β-D-mannopyranosyl units, with single (1-6) α-D-galactopyranosyl sidegroups. Low concentrations of guar gum in aqueous solution exhibit high viscosity, which changes

depending on the shear rate, showing a shearthinning or pseudoplastic behavior.[23]

Mikkonen et al. have investigated unreinforced films comprising guar gum and locust bean gum galactomannans plasticized with glycerol and sorbitol.[24] They have also investigated composite films where spruce galactoglucomannan, a by-product from thermomechanical pulping of Norway spruce, and konjac glucomannan have been reinforced with CNWs.[25,26] Mathew and Dufresne[27] and Saxena et al.[28] have used sorbitol to plasticize nanocomposite films.

In this research we present studies on a nanocomposite film consisting of a guar gum matrix with CNW reinforcement and plasticized with sorbitol. In particular, we consider the water sorption behavior. We are not aware of any studies where the water sorption kinetics behavior of such nanocomposite films has been examined, although the water sorption of cellulose membranes comprised of cellulose whiskers and microfibrillated cellulose extracted from sisal has been reported.[29] In that paper, the sorption kinetics were analyzed using both Fickian and PEK models. A Fickian model was also used to model the sorption kinetics behavior of a microfibrillated cellulose reinforced starch film[30] and a bacterial cellulose reinforced starch composite.[31] However, the use of Fickian models is generally inappropriate when sorption is associated with dimensional change of the substrate. Where swelling occurs in response to the sorption of water vapor, it is likely that relaxation limited kinetics will be observed.[32]

The sorption kinetics behavior of a range of natural materials has previously been determined within our research group by the use of a dynamic vapor sorption (DVS) apparatus with the resulting kinetic curves modeled extremely accurately using the parallel exponential kinetics (PEK) model.[33–39]

To summarize, the PEK equation has the form:

$$MC = MC_1[1 - \exp(-t/t_1)] + MC_2[1 - \exp(-t/t_2)] \quad (1)$$

where MC is the moisture content at time t; MC_1 and MC_2 are the moisture contents at infinite time and t_1 and t_2 are characteristic times for the two simultaneous kinetic processes: a fast and a slow sorption process.

In previous work it was shown that it is possible to interpret the kinetics data in terms of a relaxation limited model.[35] Under such conditions it is inappropriate to use Fickian diffusion models, since the rate limiting step is the relaxation of the polymer matrix of the sorbent and diffusion is rapid with respect to this. The relaxation of the polymer matrix represents that rate limiting step of the kinetics. The mathematical form of the fast and slow components of the PEK equation is identical to that which describes the dynamic response of a Kelvin-Voigt (K-V) element when subjected to an instantaneous stress increase of σ_0:

$$\varepsilon = (\sigma_0/E)[1 - \exp(-t/\varphi)] \quad (2)$$

where ε is the strain at time t, E is the elastic modulus and φ is a time constant which is defined as the ratio η/E, with η being the viscosity.

A change in atmospheric relative humidity (RH) leads to a response in the composite material. The maximum swelling pressure (π, here equivalent to σ_0) exerted on an elastic gel when the surrounding water vapor pressure is raised from an initial value p_i to final value p_f is given by:

$$\pi = -(\rho/M)RT \ln(p_i/p_f) \quad (3)$$

where ρ is the density of water, M is the molecular weight of water, R is the gas constant and T the isotherm temperature in Kelvin.

The strain of the system is taken to be the volume change of the material as a result of water vapor adsorption or desorption. This volume change is assumed to be linearly related to the change in the mass fraction of the water present in the material. This K-V interpretation of the data has been shown to yield values of cell wall modulus that appear reasonable for plant fibers,[35,37] cellulose[36] and wood.[34,39] Relaxation limited kinetic behavior is a commonly used interpretation in the polymer science literature, especially when considering sorption phenomena associated with polymers below their glass transition temperature (T_g).[35] It is not known how applicable such an interpretation is when examining sorption phenomena with polysaccharides and one of the objectives of this study was to determine the validity (or otherwise) of such an interpretation.

A hygroscopic sample placed in an environment at constant humidity and temperature will gain or lose moisture until it reaches the equilibrium moisture content (EMC). The relationship between EMC and RH at constant temperature is known as a sorption isotherm and materials such as cellulose exhibit a sigmoidal isotherm, classified as IUPAC Type 2. In addition the adsorption and desorption branches of the sorption isotherm follow different paths (referred to as hysteresis). The desorption EMC is always higher than the adsorption EMC and the two curves are referred to as boundary curves. If the RH is reduced, the EMC tracks across from the adsorption boundary curve to the desorption boundary curve, following what is known as a scanning curve. Similarly, if the RH is subsequently increased, the EMC will track back from the desorption to the adsorption boundary curve, but following a different path. Despite being extensively modeled, there is no consensus as to why the isotherm is sigmoidal, nor is there any generally accepted explanation of hysteresis.[31]

This laboratory recently reported on studies of the sorption behavior of cellulose, finding that the sorption kinetics was very accurately described by using the PEK model.[32] Furthermore, the sorption kinetics was described by applying a relaxation model. The purpose of this work was to further explore the applicability and interpretation of the PEK model and also to further understanding of the phenomenon of sorption hysteresis in natural materials.

EXPERIMENTAL

Materials
Cellulose nanowhiskers, were extracted from dissolving pulp by sulfuric acid hydrolysis using published methods.[8] Briefly, Whatman number one filter paper was balled-milled and sieved

through a 20-mesh screen. The ground paper (20 g) was added to 175 mL of sulfuric acid (64%, w/v) and stirred at 45°C for 1 h. The acid was removed by centrifugation and decantation. After 1 month in dialysis against running deionized water, the colloidal suspension of CNWs was diluted to 2 wt % by the addition of deionized water with constant stirring.

Industrial guar gum powder and sorbitol powder were obtained from Sigma Aldrich. A 0.5 wt % aqueous solution of guar gum was mixed, heated to 80°C and then centrifuged at 5000 rpm for 20 min to remove any undissolved guar. The resulting guar solution was clear and slightly viscous.

Method
Equal volumes (40 mL) of guar solution and cellulose nanocrystal suspension were mixed in a beaker with magnetic stirring. The guar solution and cellulose suspension gelled almost immediately to produce an opaque, viscous gel. Sorbitol (0.2–1 g; 16–50 wt % of solids) was then mixed with the gel, again with constant stirring, until completely dissolved. Air was partially removed from the gels by application of a vacuum with a diaphragm pump. The gels were cast into poly(tetrafluroethylene) petri dishes and placed in an oven to dry at 50°C for 40 h. The resulting cellulose guar composite films were easily removed from the petridishes. The films were of the order of 0.1-mm thick. They were transparent and had some small air bubbles present. There was a noticeable increase in flexibility in the films with increasing sorbitol content.

Scanning Electron Microscopy
A Hitachi S-4800 ultra-high resolution field emission scanning electron microscope (3 kV accelerating voltage; sputtering coating using platinum) was used to examine the cellulose guar nanocomposite film samples.

Dynamic Vapor Sorption
Isotherm analyses were performed using a dynamic vapor sorption intrinsic apparatus (Surface Measurement Systems, London, UK). The DVS Intrinsic comprises a measurement basket suspended from a Cahn ultrasensitive microbalance. Changes in sample mass to a resolution of 1 part in 10 million can be measured. A cellulose guar nanocomposite film (comprising 66.67 wt % CNW's, 16.67% guar and 16.67% sorbitol (dry weight) and a guar only film were finely cut. A sample of 20 mg $\pm$ 1 mg was placed into a clean sample basket which was then hooked onto the hang down wire connected to the microbalance. There was a constant flow of dry nitrogen gas through the climate controlled chamber (located in a thermostatically controlled cabinet) into which another flow of nitrogen containing water vapor was mixed to give the required preset RH values. The adsorption method for the DVS was set to RHs of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, and 95% with the reverse order for desorption. An isotherm temperature of 25°C was used. The instrument maintained the sample at a constant RH until the rate change in mass (d_m/d_t) was <0.002% min^{-1} over a 10-min period (a criterion that from previous experiments had been shown to give a sample MC to within <0.1% of the equilibrium value). Data on mass change was acquired every 20 s. Hysteresis was calculated by subtracting the adsorption EMC from the desorption EMC at a given RH.

The sample mass readings from the microbalance reveal the vapor adsorption/desorption behavior of the material. Kinetic curves for each sample were obtained by plotting percentage mass gain/loss against time, with time zero corresponding to the point at which a RH step change occurs. As a change of RH does not occur instantaneously, there is a finite time during which the RH is moving from one stable RH to the next. During this period, the MC of the sample is not moving towards a static equilibrium point, which consequently affects the initial kinetics curve. Nonlinear curve fitting with the function "ExpAssoc" [eq. (1)] was used to analyze the adsorption and desorption data curves of the nanocomposite film samples and the guar film sample, using Origin 8.1 software (Origin Lab. Corporation U.S.A). The function ExpDec1 was also used for analysis of the results where convergence of ExpAssoc proved difficult. The curve fitting procedure has been described in detail elsewhere.[40]

Dynamic Mechanical Analysis
Dynamic mechanical analysis (DMA) was performed on thin guar film samples of dimension 5 mm × 60 mm × 0.1 mm, using a TA Instruments Q800 Dynamic Mechanical Analyser and DMA-RH accessory. DMA was performed in tension mode using a dynamic oscillatory test, where a sinusoidal stress (or strain) was applied to the material and a resultant sinusoidal strain (or stress) is measured. The sample was tested using a film clamp providing open access to the film for interaction with the humidified environment. An oscillation amplitude of ±20 μm was applied to the sample at a frequency of 1 Hz. To maintain tension in the sample, a tensioning force of 130% of the oscillatory force was also applied to the sample. The measurement was performed isothermally at 25°C and the RH was scanned from zero to 95% at a rate of 1% per minute.

RESULTS AND DISCUSSION

Scanning Electron Microscopy
SEM examinations of the guar cellulose nanocomposite films plasticized with sorbitol showed good distribution of the CNWs within the matrix of the films (Figure 1).

It became apparent during the course of this work that the sorbitol could accumulate over time on the surface of the films (Figure 2). This has been noted previously by Mikkonen.[24] and was attributed to phase separation of the film-forming polymer and the plasticizer. Talja et al.[41] also noted white spots due to sorbitol crystallization on the surface of starch based films. The amount of sorbitol in the nanocomposites was accordingly reduced to below 30 wt % to prevent this occurrence.

Dynamic Vapor Sorption
As noted, the actual relative humidity (RH) takes a finite time to change to the set target RH. The mass response of the film sample to a change in RH in the sample chamber produces an asymptotic curve when plotted as moisture content against time, approaching the equilibrium moisture content (EMC) after infinite time of exposure at a given RH. The equilibrium moisture content (EMC) curves of the nanocomposite film
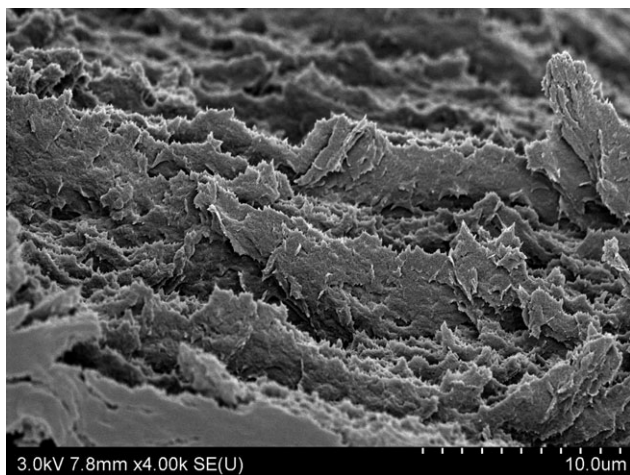
Figure 1. SEM image of the fracture surface of a guar cellulose nanocomposite film. Note the scale of 10 μm.

Figure 3. Change in moisture content of nanocomposite film and guar film against RH, showing hysteresis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

displayed slight sorption hysteresis in EMC between desorption and adsorption isotherms throughout the hygroscopic range (Figure 3). The guar only film exhibited no hysteresis above an RH of 75% and below this exhibited more pronounced hysteresis than was observed with the nanocomposite (Figure 3). When hysteresis is plotted against RH, the behavior of the guar film is more clearly illustrated (Figure 4). The guar film exhibited increasing hysteresis between 0 and 50% RH. Between 50 and 80% RH, the hysteresis rapidly decreases, approaching zero at around 75% RH. Also in Figure 4 is shown the variation in elastic modulus (obtained from the DMA study) with increasing RH. The elastic modulus decreases sharply at 75% RH, which coincides with the region in which the hysteresis collapses. This point coincides with the onset of the T_g. However, for the nanocomposite film, the trend is for a small but increasing hysteresis with increasing RH throughout the hygroscopic range, in marked contrast with the behavior of the guar film.
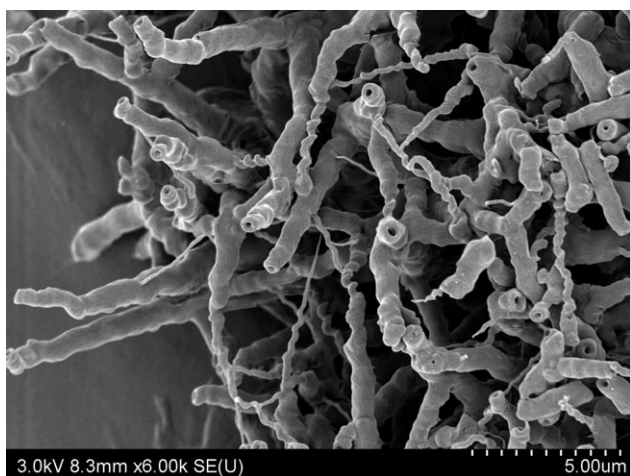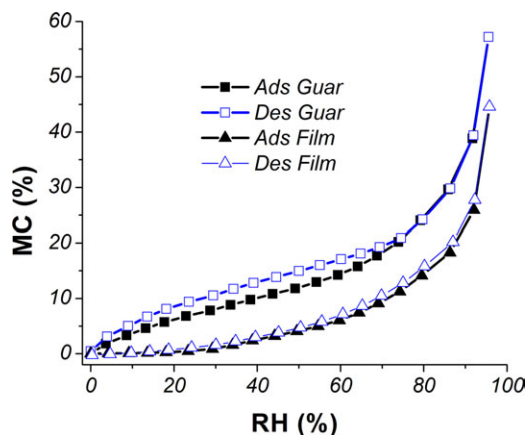
Sorption Hysteresis

It has been argued that the phenomenon of hysteresis is related to sorption occurring on polymeric sorbents below the glass transition temperature (T_g).[42] This model considers matrix relaxation under conditions of adsorption and desorption and has recently been used to explain hysteresis in natural fibers,[33,43] wood,[34,39] and cellulose.[36] Below the T_g the matrix relaxation processes are kinetically hindered because there is insufficient free volume surrounding the relaxing segments.[44,45] As water molecules penetrate the polysaccharide matrix, nanopores are created within the structure to accommodate the sorbent molecules[46] and under desorption conditions the nanopores collapse. However, due to the glassy nature of the matrix, the response is not instantaneous and consequently adsorption and desorption take place with a material that is in different states. As the T_g is approached, the relaxation events take place more rapidly, with the result that the size of the hysteresis loop decreases. At and above the T_g, hysteresis is no longer observed. Using such a model, it is possible to explain the collapse of hysteresis as being

Figure 2. SEM image of sorbitol accumulation on the surface of a guar cellulose nanocomposite film.
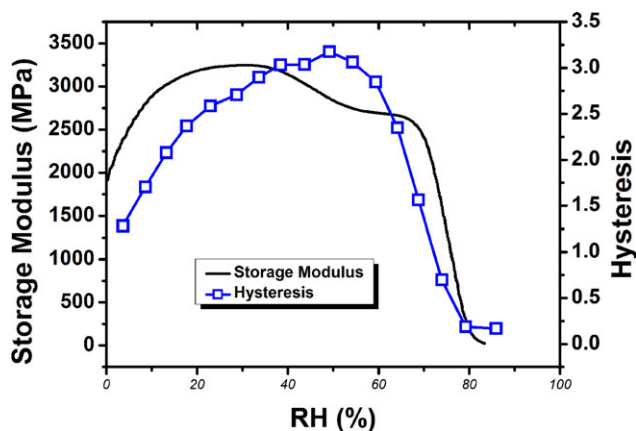

Figure 4. Hysteresis of a guar film against RH compared with the elastic modulus as determined using dynamic mechanical analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to the T_g of the guar film being reached at 75% RH at the isotherm temperature, a result that is confirmed by the dynamic mechanical analysis experiment. This model relies on certain assumptions that are listed by Vrentas and Vrentas.[42] The model considers that the thermodynamic behavior of the polymer is controlled by four variables that are independent of polymer molecular weight and that can be approximated by average values in the temperature range under consideration. It is also assumed that structural changes do not affect these variables and that rapid changes in the thermal expansion coefficient and specific heat near the T_g can be idealized as step changes. It is also assumed that the polymer-penetrant mixture, at a given penetrant concentration, exists as a nonequilibrium liquid structure below the T_g, at a particular penetrant mass fraction. It is further assumed that once such a structure is formed at a given penetrant concentration and temperature that this structure remains invariant until the penetrant concentration is changed. Other detailed assumptions are made with respect to the specific volume of the glassy polymer penetrant mixture. The purpose of this work was not to make a detailed examination of the applicability of this theory, but rather to test the simple physical hypothesis "does hysteresis collapse at T_g?". Additionally if the matrix molecular relaxation processes are responsible for the existence of hysteresis, then it was thought that it might be possible that this mechanism might also be probed through examination of the sorption kinetics processes.

The addition of the CNWs and plasticizer has a substantial influence upon the sorption behavior. Whereas the guar film exhibits a classic sigmoidal isotherm (IUPAC Type 2) and a collapse of hysteresis above 75% RH; the CNW reinforced film shows only an upward curve (IUPAC Type 3) and, as noted previously, slight hysteresis throughout the hygroscopic range. The sorption properties of the guar film and CNW reinforced film can possibly be rationalized by considering the matrix stiffness of the materials. Under conditions of adsorption (note that the term adsorption is used throughout because we are considering sorption processes associated with the internal surface of the materials) water molecules will enter the material until a state of equilibrium is established. This point being the equilibrium moisture content (EMC) at a given RH. The adsorbed water molecules apply an internal swelling pressure to the material which results in swelling of the material. Gel-like materials resist this deformation and the EMC is achieved when there is a balance between the swelling pressure and the material stiffness. The upward trend of the isotherm at higher RH values can be explained as being due to plasticization of the material by the water. With gels, the interaction between the polymers prevents infinite swelling (i.e., dissolution). The immediate explanation for the lower EMC values associated with the CNW reinforced film can thus be given as an increased modulus associated with the reinforcement. This possibility is further examined later in this article, when the sorption kinetics is discussed.

Differences in Sorption Behavior Between the Guar and Nanocomposite Film

Although the CNW fraction is a large proportion of the weight of the nanocomposite and the interior of the CNWs is not accessible to water, which may explain the lower EMCs,[33,43] the change in the shape of the isotherm is not readily explained. Some models attribute the initial part of the sigmoidal sorption isotherm as being due to monolayer formation (i.e., a Langmuir isotherm) whereas the upward curve is considered to be due to poly-layer water (the BET isotherm is one such example often used). The monolayer component is then seen as being those water molecules intimately associated with sorption sites (hydroxyl groups). The change in shape of the isotherm from sigmoidal to an upward curve has been noted when plasticizer was added to starch. Talja et al.[41] investigated the effects of sorbitol (as well as glycerol and xylitol) plasticizer content and RH on the physical and mechanical properties of potato starch-based films. At low RH, they found that films without plasticizer had higher water content than those with plasticizer. This was attributed to the films without plasticizer having more available sorption sites at low RH than films with plasticizer. Interactions (hydrogen bonds) between the hydroxyl groups of starch and hydroxyl groups of the plasticizer resulted in less sorption sites in the plasticized films. Hence the change in shape of the isotherms can be attributed to the presence of plasticizer. However, plasticized films also exhibit much increased moisture contents over unplasticized films in the upper end of the hygroscopic range, which was not observed with the experiments described herein. It is therefore likely that in the case of cellulose guar films plasticized with sorbitol, the reduction in adsorbed water of the film over the entire hygroscopic range is due to a combination of the addition of the CNW's (upper range) and the presence of the plasticizer (lower range). It is also interesting to note that the CNW reinforced film exhibits a small but measureable hysteresis throughout the hygroscopic range. Films cast directly from CNWs or from microfibrillated cellulose have been shown not to exhibit any sorption hysteresis,[29] which is presumably due to a lack of any matrix material. It is possible that the existence of sorption hysteresis observed in the experimental work reported herein is caused by an antiplasticization effect caused through interaction between the sorbitol and the other two components of the film.[41] Work is continuing to further understand this tentative hypothesis.

Parallel Exponential Kinetics (PEK)

The PEK model was used to examine the sorption kinetics. The characteristic times, t_1 and t_2, for the two simultaneous fast and slow kinetic processes were obtained from nonlinear curve fitting of eq. (1). For any 5% RH stage of sorption or desorption, the initial data points in the curve for that stage are associated with conditions of rapidly changing RH. The characteristic times for any fit including the first few points will therefore not be representative of the material properties and thus they were removed from the fit. However, as more points are excluded from the curve fitting process, the values for the mass changes for the fast and slow kinetics process could become less accurate. In practice, removal of up to the first three data points was sufficient to obtain a good quality curve fit.

For the nanocomposite films, the curve fitting procedure typically did not converge above 85% RH. It could also prove difficult to achieve convergence between 0 and 10% RH, in

some cases. This suggests that the sorption kinetics is different in the upper and lower parts of the hygroscopic range and was further confirmed by the satisfactory fitting of a single exponential function where convergence of the two part exponential function was not achieved.

For the guar film, convergence of ExpAssoc, the two part exponential equation, was not achieved above 60% RH for adsorption and 70% RH for desorption This coincides with the sudden decrease in hysteresis observed above 75% RH and may correspond to the T_g of the guar film being the isotherm temperature at that EMC. To further investigate this change, a single exponential curve fit (ExpDec1) was used. Above 70% RH the single exponential equation gave good curve fitting results, below 70% RH the double exponential equation gave much better convergence than the single exponential. A mechanical (i.e., relaxation limited) model for the sorption kinetics is given below. The above results indicate that two simultaneous relaxation processes occur below the T_g, but that there is only one above the T_g. The significance of this result is unclear at present, but may suggest that the two kinetic processes (i.e., fast and slow) may represent two fundamentally different physical phenomena.

Interpretation of Sorption Kinetics based on the Kelvin–Voigt Model

If a relaxation limited sorption kinetics process is assumed, then the data obtained from the PEK model can be used to calculate modulus of elasticity of the matrix of the nanocomposite material or guar film. The sorption kinetic parameters were used as input into eq. (2), with the swelling pressure associated with each measured RH incremental step calculated according to eq. (3).

The variation in matrix modulus related to the fast and slow adsorption kinetic process obtained from the K–V analysis is presented in Figure 5 for the guar film and these data are compared with the elastic modulus values determined from the
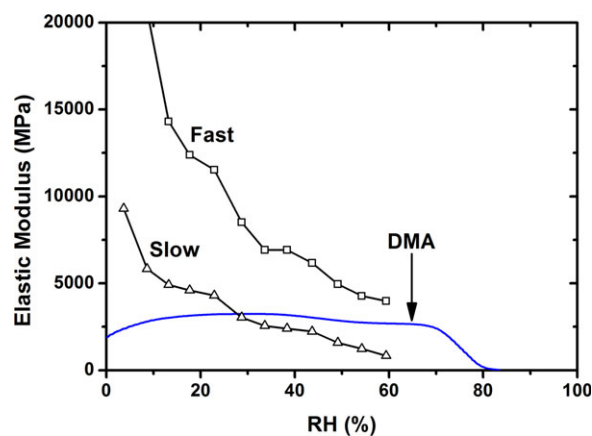

Figure 5. Comparison of elastic modulus as determined using dynamic mechanical analysis and modulus associated with the fast and slow kinetic adsorption processes determined using the Kelvin-Voigt model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DMA experiment. The K–V derived values of the modulus both show distinct downward trends as the RH increases; behavior that is not observed with the DMA data. Furthermore, the values of the elastic modulus obtained using the K–V analysis are higher by a considerable margin (especially with the data associated with the slow process) at the lower end of the hygroscopic range, compared with the values found from the DMA analysis. The downward trend in the K–V derived data may represent an artifact arising from the logarithmic relation used to calculate the internal swelling pressure caused by the sorbed water at different RHs. It is also important to consider that the modulus calculated from the K–V analysis represents a value derived from an internal pressure and, as such, cannot be directly be compared with a parameter obtained by the application of an external force (as is the case with DMA). The K–V model also makes the simple assumption that the MC is solely controlled by the internal modulus of the material, whereas it is highly likely that internal accessibility of the material is also a significant factor. For example, when similar analysis was performed on the nanocomposite film, modulus values as high as 200 GPa were obtained at the lower end of the hygroscopic range. Such a value exceeds that of the tensile modulus of a CNW and cannot be considered to be realistic.

The phenomenon of sorption hysteresis in a natural material such as cellulose has been explained by consideration of the sorption process in a glassy polymer matrix. Nanopores are created during the adsorption process and collapse during the desorption process.[36] The rate of response of the matrix to sorption is dependent upon the mobility of the constituent molecules and therefore determined by the glass transition temperature (T_g), below which the matrix is unable to respond instantaneously to the movement of the sorbent molecules. Sorption hysteresis arises because of this time lag in the response of the matrix on time scales relevant to molecular diffusion processes. With sorbent molecules entering the material there is less void volume in the matrix, compared with the situation where the molecules are leaving the material.[38] Adsorption and desorption therefore occur with a material that is in different states. This then implies that the phenomenon of hysteresis and the dynamic sorption behavior are linked.

It is striking that the change in the equilibrium behavior and dynamic behavior may be linked in this way and it has previously been proposed that the sorption kinetics behavior can be linked to the phenomenon of hysteresis by consideration of matrix relaxation.[37] This then may perhaps give an insight into what the fast and slow processes represent. Dual relaxation terms are usually interpreted in the polymer literature as being due to two components (i.e., copolymers, side plus main chain relaxations, etc.). In the guar film it appears that the slow relaxation term is associated with the glassy state.

CONCLUSIONS

Addition of cellulose nanowhiskers (CNWs) to guar in the presence of sorbitol as a plasticizer produced flexible films, although

high levels of sorbitol did not give films with long term stability. The water vapor sorption behavior of the guar films was dramatically different when the CNWs and sorbitol were present. Whereas the guar film exhibited a sigmoidal (IUPAC Type 2) isotherm, that of the CNW reinforced film showed a continuous upward increase (IUPAC Type 3). The CNW reinforced films demonstrated very low levels of absolute hysteresis, but hysteresis was observed throughout the hygroscopic range and increased slightly as the RH increased. By contrast the guar only film exhibited relatively high levels of hysteresis, but this decreased as the RH was raised and disappeared at around 75% RH. At this point the sorption kinetic behavior was also found to change, with a PEK model proving adequate below this RH but a single exponential function being more appropriate above. The region of collapse of the sorption hysteresis in the guar film coincided with the onset of the glass transition temperature.

ACKNOWLEDGMENTS

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