

A Multivariant Study of the Absorption Properties of Poly(glutaric acid-glycerol) Films

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ABSTRACT: Hydrogels and organogels are polymer networks that can absorb large amounts of water and organic solvent, respectively. In this study, solvent absorption into the matrices of poly(glutaric acid-glycerol) hydrogel and organogel films amended with or without either iminodiacetic acid, sugarcane bagasse, pectin, corn fiber gum, or microcrystalline cellulose has been evaluated. Most of the starting materials used in this study, such as glycerol and the plant wall polysaccharides, are by-products of biofuel production. Finding uses for them would further biofuel initiatives worldwide. To that end, experimental results showed that water absorption increased when using polymer films composed of additional glycerol or plant cell wall polysaccharides. The amount of solvent absorbed into the control film increased when incubated in pH 10 buffer solutions but decreased when incubated in pH 4 buffer solutions and NaCl solutions when compared with absorption of water. Incubating the polymers in solvent at elevated temperatures increased the absorption rate. It was determined that the combined effects of pKa and polarity can be used to predict solvent absorption. Dimethylsulfoxide (DMSO) could be selectively extracted from or desorbed into films from other solvents. Erosion of the polymer films in DMSO ranged from 1.9 (± 0.2) to 34.7 (± 3.4)%. In water, erosion ranged from 6.3 (± 3.2) to 32.7 (± 3.2)%. The polymer films resorbed 3.3- and 2.3-fold more DMSO and water, respectively, when compared with the original amount of absorbed solvent. These materials are potentially good candidates for agricultural and medicinal applications because their ability to absorb, desorb, and erode can be tuned. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 70–77, 2013

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INTRODUCTION

Polymeric films are three-dimensional networks that, dependent on their chemical composition, have the ability to behave as hydrogels or organogels by absorbing large amounts of water or organic solvent, respectively. They are composed of amorphous and crystalline regions that cannot dissolve but swell in the presence of solvents. They inherently respond to changes in solvent composition,^{1–3} pH,⁴ temperature,⁵ and salt concentrations⁶ or they can be engineered to respond to various environments by changing their molecular composition or altering their polarity or ionic properties through functionalization.

The swelling behavior of polymeric films can be affected by several forms of external stimuli including pH, ionic strength, and applied electrical or magnetic fields due to the resulting changes in network structure, permeability, and mechanical strength.⁷ The effect of pH on materials is an important parameter to consider when designing products to be used in the controlled delivery of bioactive substances⁸ and for soil and water

preservation.⁹ In these applications, the ability of materials to release compounds and solutions by deswelling is just as important as their ability to absorb and retain them. Several examples exist in the literature to show that pH can affect the swelling and deswelling of polymer films. Pectin-derived hydrogels were shown to swell in solutions of high pH and deswell at low pH¹⁰ and the rapid deswelling of a polymer film was effective in facilitating the release of lysozymes.¹¹ In other studies, pH-dependent swelling has also been shown to arise from acidic pendant groups in the polymer network.¹² Such findings suggest the potential value on characterizing the pH-dependent swelling behavior of polymers made with glutaric acid as reported here.

In an effort to find uses for the excessive amount of glycerol generated during biodiesel production, we have previously prepared poly(glycerol-co-diacid) films and determined that they have the potential to be used as polymeric absorbent gels.¹³ The films were able to absorb various amounts of a variety of solvents without compromising their elasticity. The results of those

initial investigations revealed that aprotic polar solvents such as DMSO and THF were more readily absorbed than polar solvents such as water and methanol. Hexane, the only nonpolar solvent investigated in the previous study, was not absorbed into the polymer films. The amount of solvent absorbed for the polar solvents ranged greatly from, on average, 9.5% for water and 261% for DMSO.

It is our desire to improve the efficiency of water absorption in these types of polymers. It is possible to increase the amount of water absorbed into the polymer films by adding hydrophilic additives. Upon the suggestion of fellow researchers who are experts in the utilization of coproducts from the production of ethanol, crude and purified plant cell wall polysaccharides were deemed suitable additives for this study. Mixing agriculturally derived coproducts (sugarcane bagasse), biopolymers isolated from coproducts [pectin, microcrystalline cellulose, or corn fiber gum (CFG)] or iminodiacetic acid (IDA) into the polymer matrix before curing could enhance water absorption. IDA is a short-chain dibasic acid that can be produced by biocatalysis.¹⁴ It is not a plant cell wall polysaccharide; however, we have shown that it reacts with glycerol to form a water-soluble gel.¹⁵ In addition, Iyer et al. found that IDA derivatives can form hydrogels that swell when thermally stimulated.¹⁶

Sugarcane bagasse, a by-product plant material that remains after sucrose is harvested from sugar cane, has been used to improve the water absorption in low-density polyethylene thermoplastic resins.¹⁷ It is composed of ~40% cellulose, 24% hemicellulose, and 25% lignin giving it the ability to also serve as good reinforcement for polymer composites.¹⁸ Pectin, a polysaccharide structural component of plant cell walls, is nontoxic and is a promising candidate as a composite material in controlled released formulations that have shown a high degree of swelling and slow drug release.¹⁹ Similar results have been observed for microcrystalline cellulose.²⁰ There was no literature available on the use of CFG, the water-soluble arabinoxylan (hemicellulose) fraction isolated from corn kernels. However, it has been used as an additive to produce biobased films.²¹

In the present study, H₂O, the solvent that was least absorbed, and DMSO, the solvent that was most absorbed by polymer films made from glycerol and glutaric acid, will be used to evaluate the absorption properties of these films following their amendment with various plant cell wall polysaccharides and IDA. DMSO is a very common, nontoxic, highly polar organic solvent that is well studied as a pharmaceutical agent.^{22,23} While polymers that absorb DMSO have myriad applications, the ability to absorb water is just as important. In fact, hydrogel research is extensive and has led to uses in food, agriculture and medicine.^{9–11} These applications include superabsorbent materials,¹² sensors,²⁴ transport,²⁵ drug delivery,²⁶ and water remediation.²⁷ Therefore, the primary intent of this investigation is to vary the composition of the glutaric acid–glycerol polymers in an effort to produce polymer films that absorb more water than previously observed. It is also of interest to observe if changes in polymer film composition positively or negatively affect DMSO absorption. In addition, the affects of absorption resulting from changes to the chemical nature of the surrounding media were investigated.

EXPERIMENTAL

Materials

Glutaric acid (99%), reagent grade glycerol (99.9%), HPLC grade toluene (99.8%), reagent grade *t*-butyl acetoacetate (98%), and spectrophotometric grade dimethylsulfoxide (DMSO) were purchased from Sigma Aldrich (St. Louis, MO). Sodium chloride crystal was purchased from J.T. Baker (Phillipsburg, NJ). HPLC grade acetone and hexanes (certified ACS) were purchased from Fischer Scientific (Fair Lawn, NJ). HPLC grade ethyl acetate was purchased from Burdick and Jackson (Muskegon, WI). Deionized water was obtained from our in-house Barnstead NANOpure (Boston, MA) system. Aluminum weighing dishes (4" dia. × 5/16" deep) and jars (Qorpak, 2 oz, Straight Side Round Jars with Teflon-Lined Caps) were purchased from Thomas Scientific (Swedesboro, NJ). Sugarcane bagasse (dominant variety HoCP 96-540) was provided by colleagues at the Southern Regional Research Center, U.S. Department of Agriculture (New Orleans, LA) who had obtained it from Raceland Raw Sugars Corporation (Raceland, LA). Pectin (type X-939-04) was purchased from CPKelco (Atlanta, GA). Avicel microcrystalline cellulose (Lattice NT-020) was received as a gift from FMC Biopolymer (Philadelphia, PA). Corn fiber was provided by ADM Research, which was oven dried by the supplier before shipping. Fiber samples were ground to a 20-mesh particle size using a Wiley mill and extracted with hexane to remove oil. Starch was removed from the 20-mesh de-oiled fiber by treating with Termamyl α -amylase (a gift from Novo Nordisk Bioindustrials, Inc., Danbury, CT).²⁸ Buffer solutions [pH 4 (made with potassium acid phthalate in water) and pH 10 (made with sodium bicarbonate and sodium bicarbonate in water)] were purchased from VWR International, Inc. (West Chester, PA). Indicator strips (pH 5.0–10.0) were obtained from EMD Chemicals (Gibbstown, NJ).

Synthesis of Polymer Films

Polymer films were made by first synthesizing polymers from glycerol and glutaric acid using a modified version of a previously described protocol.¹³ A 2: 1 molar ratio of glutaric acid (1.4 mol) and glycerol (0.7 mol) or a 1: 2 molar ratio of glutaric acid (0.7 mol) and glycerol (1.4 mol) were reacted in a 1-L round-bottom flask with 460 mL of toluene. Syntheses were performed at oil bath temperatures of 135°C for 6 h. A reflux condenser was connected to the top of a Dean-Stark apparatus used to assist in the removal of water generated over the course of the esterifications. Following reaction, the solvent was removed from the crude reaction products by rotary evaporation. These polymers were used to make films that would further react to consume any residual starting material. Therefore, purification at this step is deemed unnecessary.

The reaction mixture (15 g) consisting of a 2: 1 molar ratio of glutaric acid: glycerol were transferred to individual aluminum weighing dishes and cured in an oven at 135°C for 12 h. Additional films were made from 20% (w/w) blends of either IDA, pectin, sugarcane bagasse, CFG, and microcrystalline cellulose by manually adding and mixing 3 g of each substance into 12 g of the 2: 1 (glutaric acid: glycerol) polymer gel. To study the effects of additional amounts of glycerol, 15 g of the reaction mixture consisting of a 1: 2 molar ratio of glutaric acid: glycerol

were transferred to individual aluminum weighing dishes and cured in an oven at 135°C for 24 h. The pre-cured polymers were characterized by FTIR¹² and NMR²⁹ (¹H and ¹³C) as previously described.

Isolation of Corn Fiber Gum

CFGs were isolated from deoiled and destarched corn fiber by alkaline hydrogen peroxide technology.³⁰ In brief, deoiled and destarched corn fiber was mechanically stirred into an alkaline solution containing 0.088M NaOH and 0.026M of Ca(OH)₂ in the presence of 0.63% aqueous H₂O₂ at boiling temperature for 1 h with maintaining pH about 11.5 by adding more NaOH. The reaction mixture was centrifuged at 6000 × *g* for 30 min after cooling it by stirring at room temperature, and the supernatant was separated from the residue by decantation. The residue was resuspended in water and boiled for 5 min with mechanical stirring. The reaction mixture was centrifuged as above and the supernatant was decanted and mixed with the first supernatant. The pH of the combined supernatant (alkaline H₂O₂ extract) was then adjusted to 4.0–4.5 by adding HCl to precipitate hemicellulose A, which was collected by centrifugation at 10,000 × *g* for 1 h. Two volumes of ethanol were gradually added to the supernatant with stirring to precipitate the hemicellulose B, (CFG), which was collected and dried.

Absorption and Erosion Measurements

Procedure and Calculations. The samples were bored from the aluminum pans into circles that were 1 inch in diameter. The samples were weighed and immersed into 15 mL of solvent at room temperature and weighed at predetermined intervals of time up to 24 h in capped, 2 oz jars. The samples were removed from the jars at specific times, blotted with a Kimwipe (Kimberly-Clark, Marietta, GA), weighed, and returned to the jar until the time of the next measurement. Similar studies were performed at room temperature in pH 4 and pH 10 buffer solutions, 10 and 20% salt (NaCl) solutions and also at 40 and 80°C in a temperature-controlled Thermo Scientific (Waltham, MA) Thermolyne furnace.

Weight changes due to solvent absorption were determined by the following equation:

$$\% \text{ Weight change} = (W_s - W_d)/W_d * 100 \quad (1)$$

where W_s and W_d represent the weight of the swelled and dry films, respectively. Erosion resulting from the degradation of the polymer gel was determined by the following equation:

$$\% \text{ Erosion} = (W_o - W_{de})/W_{de} * 100 \quad (2)$$

where W_o and W_{de} represent the weight of the preswelled and desorbed films, respectively.

Polymer Resorption. To evaluate the ability to reuse these materials, the polymer films were allowed to desorb by gravity filtration in fume hoods until the polymer films no longer lost weight. The desorbed polymer films were then resubmerged into solvent and evaluated for solvent absorption as previously described using eq. (1).

Preferential Solvent Extraction from Mixtures. To evaluate the ability of these materials to extract DMSO from miscible and immiscible systems, 1 mL (1.1 g) of DMSO was added to 14 mL of hexane, *t*-butyl acetoacetate, or water and incubated in capped, 2 oz jars for 24 h. Samples were examined for solvent absorption as previously described using eq. (1).

Solvent Desorption from Polymer Films into Surrounding Media. To evaluate the ability of these materials to desorb solvents, films with previously absorbed DMSO or pH 10 buffer were incubated in DI H₂O, pH 4 buffer, or pH 10 buffer. Samples were removed from the solvent, blotted dry and weighed at 15 min, 10, and 24 h. Percent desorption was calculated using eq. (1).

Scanning Electron Microscopy (SEM)

The samples (5 × 10 mm) were dehydrated by three successive 60-min incubations in 20-mL volumes of 50, 80 vol %, and absolute ethanol. The samples were then frozen in liquid nitrogen and fractured with cold scalpel blades. The samples were critical point dried from liquid CO₂ in a DCP-1 Critical Point Dryer (Denton Vacuum, Inc., Cherry Hill, NJ). The samples were mounted on specimen stubs using carbon adhesive tabs. The edges of the samples were then painted with a colloidal silver adhesive (Electron Microscopy Sciences, Hatfield, PA). Finally, the samples were sputter coated with a thin layer of gold using a Scaicoat Six Sputter Coater (BOC Edwards, Wilmington, MA).

Digital images of topographical features of the samples were collected using a Quanta 200 FEG environmental scanning electron microscope (FEI, Co., Inc., Hillsboro, OR) operated in the high vacuum/secondary electron imaging mode at an accelerating voltage of 10 kV and instrumental magnifications of 50×, 250×, 500×, and 1000×.

RESULTS AND DISCUSSION

Synthesis

Polymers made from esterifications between glycerol and glutaric acid were prepared by modifying our published synthetic protocol.¹³ As expected, the 6 h synthesis in toluene at 135°C gave polymer gels in the form of viscous liquids. Using a previously described method for NMR analysis,²⁹ degrees of branching of 54.9 and 0.0%, respectively, were determined for polymers made from 2: 1 or 1: 2 molar ratios of glutaric acid and glycerol. A degree of branching of 0.0% was unexpected but aligns perfectly with previously determined values for degree of branching of 25% for a 1: 1 formulation of polymers of the same type.¹³ Consistent with the solubility characteristics of similar polymers,^{12,15} these polymers were soluble in polar organic solvents but would not dissolve in water or nonpolar solvents.

The polymer gels were cured at 135°C and checked regularly to monitor the loss of tackiness throughout the entire film. After 12 h, the polymers were solid films that could be removed from the aluminum pans without any qualitative degree of tackiness. The polymers made with a 2: 1 (glutaric acid: glycerol) molar ratio, with and without additives, lost an average of 8.8 (±0.7)% of its initial weight, presumably in the form of water

as the by-product of esterification. The polymer made with a 1: 2 (glutaric acid: glycerol) molar ratio lost an average of 24.1 (± 2.3)% of its initial weight. The final products were flexible solids that were easy to cut. The polymers devoid of additives were clear with a yellow hue. The polymer films infused with additives were opaque films in various shades of brown.

Absorption Studies

Previous studies on the absorption of solvents into polymers made from a 2: 1 molar ratio of glutaric acid and glycerol revealed that, of the polar solvents tested, DMSO and water were absorbed the most and the least, respectively.¹³ To improve the hydrogel character of the polymer films, plant cell wall polysaccharides, IDA and additional amounts of glycerol were added to the polymer formulations before curing. In these studies, the 2: 1 (glutaric acid: glycerol) polymer film serves as the control polymer. Therefore, all observations are relative to that formulation (Table I). The addition of microcrystalline cellulose and sugarcane bagasse showed no improvement over the control polymer when incubated in DI H₂O for 24 h. However, the incorporation of pectin and changing the molar ratio from 2: 1 (glutaric acid: glycerol) to a 1: 2 formulation improved the absorption of water by ~ 3.3 -fold. The most significant improvement in water absorption was observed with the CFG-infused polymer, which absorbed 35.4 (± 8.8)% of its weight showing a 6.7-fold increase over the absorption by the control polymer which absorbed only 5.3 (± 0.3)% of its weight. When IDA was cured into the matrix of the polymer film, it initially absorbed a small amount of water before showing weight loss. We have previously shown that iminodiacetic and glycerol produce a water-soluble polymer.¹⁵

Additions to the matrix of the polymer films did not improve their ability to absorb DMSO. Within error, the 1: 2 (glutaric acid: glycerol) polymer films and the composite films made with CFG, IDA, and pectin showed no change in DMSO



Figure 1. Illustration of dry poly(glutaric acid-glycerol) microcrystalline cellulose composite film (left) and poly(glutaric acid-glycerol) microcrystalline cellulose composite films after absorbing water (middle) or DMSO (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption after 24 h relative to the control. However, the rate at which they absorbed DMSO until reaching their maximum varied. The addition of sugarcane bagasse and microcrystalline cellulose resulted in a 25% decrease in DMSO absorption when compared with the control. It is also observed that maximum absorption was achieved at 10 h and desorption or degradation began to occur thereafter. An example of polymer films absorbed separately in water and DMSO are illustrated by their pictures in Figure 1.

The control polymer film was tested at elevated temperatures to see if a correlation existed between temperature and absorption (Table II). When compared with solvent absorption at room temperature, it was clear that increasing the temperature does not increase the solvent capacity of the films but it does increase the rate of absorption. After 1 h at 80°C, the absorption maximums were reached. The time to reach maximum water absorption was 18 h at room temperature, 3 h at 40°C and 1 h at 80°C. It took 10 h to reach maximum DMSO absorption at room temperature, 3 h at 40°C and 1 h at 80°C.

Table I. Percent Absorption of Water or DMSO into the Polymer Matrix of Poly(glutaric acid-glycerol)-Based Films

Additives	0 h	1 h	3 h	10 h	18 h	24 h
% Absorption in water						
2: 1 Glutaric acid: glycerol	0.0	1.8 (± 1.3)	3.1 (± 0.8)	4.0 (± 0.8)	5.3 (± 0.3)	5.3 (± 0.3)
1: 2 Glutaric acid: glycerol	0.0	9.1 (± 0.9)	15.0 (± 0.4)	20.9 (± 0.2)	19.2 (± 0.3)	18.0 (± 0.1)
Corn fiber gum	0.0	14.2 (± 3.8)	26.3 (± 3.3)	41.9 (± 10.6)	37.8 (± 10.8)	35.4 (± 8.8)
IDAA	0.0	0.5 (± 0.2)	1.0 (± 0.1)	0.0 (± 0.2)	-1.0 (± 0.1)	-3.0 (± 0.4)
Microcrystalline cellulose	0.0	2.6 (± 0.2)	4.0 (± 0.5)	5.3 (± 0.3)	5.3 (± 1.3)	5.3 (± 1.8)
Pectin	0.0	11.2 (± 0.9)	16.7 (± 3.4)	21.7 (± 7.8)	22.7 (± 6.5)	17.5 (± 9.9)
Sugarcane bagasse	0.0	2.6 (± 0.3)	5.2 (± 0.6)	7.3 (± 0.4)	7.8 (± 2.3)	7.8 (± 2.3)
% Absorption in DMSO						
2: 1 Glutaric acid: glycerol	0.0	101.3 (± 17.3)	183.9 (± 15.3)	236.4 (± 2.9)	234.0 (± 0.9)	230.5 (± 1.0)
1: 2 Glutaric acid: glycerol	0.0	68.7 (± 23.0)	148.4 (± 24.3)	215.1 (± 13.4)	217.4 (± 19.7)	216.1 (± 13.2)
Corn fiber gum	0.0	136.1 (± 2.3)	224.9 (± 24.1)	244.3 (± 32.2)	236.9 (± 26.2)	234.2 (± 17.3)
IDAA	0.0	129.0 (± 25.0)	209.8 (± 10.4)	229.7 (± 12.2)	229.9 (± 13.3)	224.0 (± 11.2)
Microcrystalline cellulose	0.0	75.1 (± 17.6)	164.4 (± 4.9)	175.1 (± 13.6)	174.1 (± 13.4)	173.0 (± 14.2)
Pectin	0.0	225.2 (± 6.2)	267.0 (± 24.5)	278.6 (± 35.4)	270.7 (± 36.5)	264.5 (± 35.3)
Sugarcane bagasse	0.0	117.9 (± 18.2)	188.3 (± 20.8)	181.2 (± 0.2)	177.5 (± 0.8)	171.7 (± 0.4)

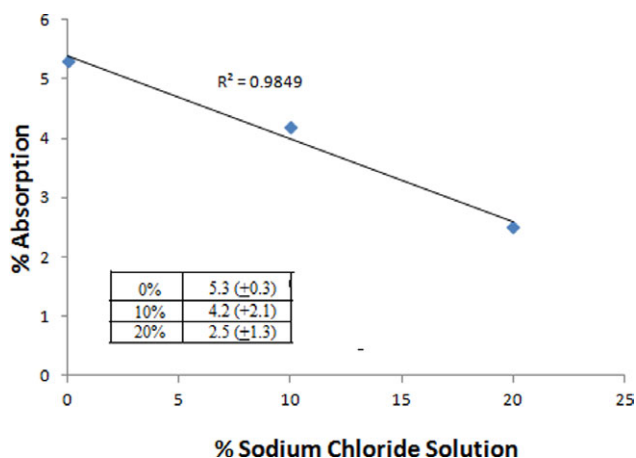
Table II. Absorption of Water or DMSO by the Control Polymer Film at 40 and 80°C

Temperature (°C)	0 h	1 h	3 h	10 h	18 h	24 h
% Absorption in water						
RT	0	1.8 (± 1.3)	3.1 (± 0.8)	4.0 (± 0.3)	5.3 (± 0.3)	5.3 (± 0.3)
40	0	4.0 (± 0.2)	5.5 (± 0.4)	4.0 (± 2.3)	2.5 (± 0.6)	2.0 (± 0.1)
80	0	5.3 (± 1.0)	2.1 (± 1.3)	n/a	n/a	n/a
% Absorption in DMSO						
RT	0	101.3 (± 7.6)	183.9 (± 9.6)	236.4 (± 2.9)	234.0 (± 0.9)	230.5 (± 1.0)
40	0	156.6 (± 7.7)	235.5 (± 4.7)	225.3 (± 6.6)	219.7 (± 3.5)	214.0 (± 8.5)
80	0	231.3 (± 0.3)	225.0 (± 5.5)	218.0 (± 10.6)	218.0 (± 10.6)	202.9 (± 8.5)

The film morphed from a solid to a gel at 80°C in water between the 3 and 10 h incubation periods.

The effects of the chemical properties of the solvent were examined by varying the pH of the liquid medium (Table III) and salt concentration (Figure 2) of the solvent. With the exception of the weight of the polymer absorbed at 24 h in pH 4 buffer, absorption increased incrementally with time as a function of pH (Table III). At pH 4, the absorption of water by the polymer film decreased relative to that at pH ~ 6 . When the pH was increased to 10, the film absorbed more water. To study the effects of salt concentration on absorption, the control polymer film was incubated for 24 h in 10 and 20% sodium chloride solutions. A linear inverse correlation was observed between the absorption of aqueous solution and the salt concentration of that solution (Figure 2) suggesting that the interactions between the water and NaCl ions are stronger than the interactions available to the water within the polymer film matrix.

In our previous work, we learned that there was no correlation between the polarity and the degree of absorption of a solvent, but that aprotic polar solvents [i.e., DMSO and tetrahydrofuran (THF)] were better absorbed into poly(glutaric acid-glycerol) films than protic solvents (i.e., MeOH and H₂O).⁷ The present study indicates pKa is a better indicator for solvent absorption than polarity (Table IV). However, combining the effects of polarity with the pKa of a solvent may be useful when attempting to design a predictive model. In general, as the pKa increased, the percent absorption also increased. However, as shown in Table IV, when the pKa values of two solvents are similar, the solvent with the greater polarity absorbs more solvent. For example, THF has the highest pKa (38) of the solvents used in this study followed by DMSO (pKa = 35). However, DMSO, with a higher polarity [Snyder Polarity Index (SPI)³¹ = 6.5] is absorbed in greater amounts than THF (SPI = 4.2). The same is exemplified when comparing acetone (pKa = 20) and ethyl acetate (pKa = 21). They have similar pKa values but acetone,

**Figure 2.** Percent absorption of 10.0 and 20.0% sodium chloride solutions into 2:1 glutaric acid:glycerol polymer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with a higher polarity (SPI = 5.4), is absorbed in greater amounts than ethyl acetate (SPI = 4.3). The polar aprotic solvents, H₂O and MeOH, were again, the least absorbed. They have high polarities (H₂O = 9; MeOH = 6.6) but lower pKa values than the aprotic solvents. Further suggesting that pKa is a good indicator for absorption, only a small amount of the aprotic solvent, *t*-butyl acetoacetate (pKa = 10), was absorbed into the polymer. Hexane, which is nonpolar (SPI = 0), was not absorbed at all.

Preferential Solvent Extraction from Mixtures

Experiments were designed to determine if DMSO could be extracted from other solvents into the control film (Table V). For this study, 1 mL of DMSO was added to low absorbing solvents (hexane, water, and *t*-butyl acetoacetate) and incubated for 24 h. The total weights of the films were expected to increase by 1.1 g if all of the DMSO was extracted. The data

Table III. Percent Absorption of pH 4 or pH 10 Buffer Solutions into the Polymer Matrix of 2:1 Glutaric Acid:Glycerol Polymer Films

	0 h	1 h	3 h	10 h	18 h	24 h
pH 4	0.0	1.3 (± 0.6)	1.8 (± 1.3)	3.6 (± 2.6)	3.9 (± 2.6)	2.8 (± 2.6)
DI water (pH ~ 6)	0.0	1.8 (± 1.3)	3.1 (± 0.8)	4.0 (± 0.3)	5.3 (± 0.3)	5.3 (± 0.3)
pH 10	0.0	10.6 (± 0.6)	19.2 (± 1.7)	24.2 (± 0.3)	30.8 (± 0.4)	33.4 (± 4.8)

Table IV. Solvent Absorption as a Function of pKa and Polarity (as Designated by the Snyder Polarity Index (SPI))

Solvents	pKa	SPI	24 h
Hexane ⁷	n/a ^a	0.0	0.0 (± 0.0)%
<i>t</i> -Butyl acetoacetate	10	n/a ^a	5.8 (± 0.8)%
Water	15.7	9.0	5.3 (± 0.3)%
MeOH ⁷	16	6.6	33.0 (± 2.1)%
Acetone	20	5.4	92.0 (± 6.5)%
Ethyl acetate	21	4.3	49.9 (± 2.2)%
DMSO	35	6.5	230.5 (± 1.0)%
THF ⁷	38	4.2	131.0 (± 6.3)%

^aLiterature value for this parameter was not found.

shows that in nonpolar solvent (hexane) the polymer film extracted $88.2 \pm 0.2\%$ of the theoretical maximum amount of DMSO. It was followed by *t*-butyl acetoacetate ($37.0 \pm 5.6\%$) and water ($1.4 \pm 0.7\%$). It is easy to understand why DMSO is easily extracted from hexane as they form two immiscible phases. However, preferential solvent extractions of DMSO from water and *t*-butyl acetoacetate were also expected. It is unclear why those solvents retard the absorbance of DMSO into the polymer matrix. However, these observations for DMSO and water are likely due to their strong intermolecular interactions⁸ and miscibility.

Solvent Desorption from Polymer Films into Surrounding Media

DMSO was absorbed into the control film by incubation for 24 h. The films swollen by DMSO were weighed and subsequently incubated in DI H₂O or either pH 4 or pH 10 buffer solutions. Within 15 min, the polymer films containing DMSO had lost 73.8, 71.8, and 71.5% of its weight in DI H₂O, pH4 buffer, and pH 10 buffer, respectively (Figure 3). The desorption percentages equilibrated at $\sim 80\%$ in DI H₂O and pH 4 buffer. However, the film resorbed solvent in the pH 10 buffer solution to regain the weight that it had initially lost. The chemical nature of the swelling–deswelling cycles is unknown and it is also unclear whether DMSO or pH 10 buffer was the reabsorbed solvent.

CFG composite films showed the highest degree of absorbance of water. Therefore, they were chosen for desorption studies and

Table V. Percent Absorption of DMSO by Extraction with Poly(glutaric acid-glycerol) Films from Low Absorbing Solvent Systems after 24-h Incubations

Solvents	w/o DMSO	w/ DMSO	% Extracted ^a
Hexane	0.0 (± 0.0)%	122.8 (± 0.8)	88.2 (± 0.2)
<i>t</i> -Butyl acetoacetate	5.8 (± 0.8)%	47.1 (± 4.7)	37.0 (± 5.6)
Water	5.3 (± 0.3)%	2.0 (± 1.0)	1.4 (± 0.7)

^aBased on theoretical expectation of 1mL (1.1g) DMSO.

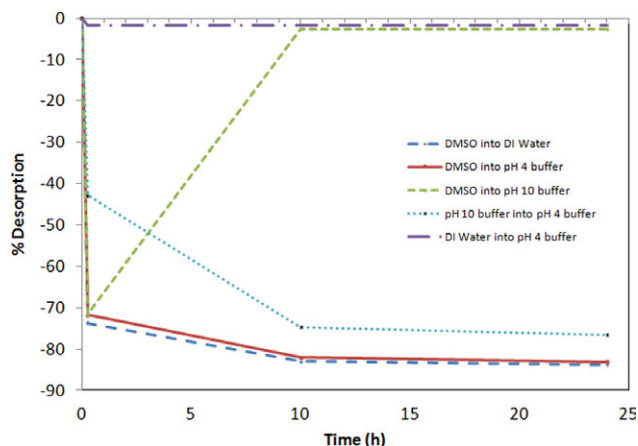


Figure 3. Solvent desorption of DMSO from the control polymer film and desorption of pH 10 buffer and DI H₂O from corn fiber gum composite films into surrounding media. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were incubated in DI H₂O and pH 10 buffer solution for 24 h. As expected (Table I), the CFG film absorbed 51.5% of its weight in water but it absorbed 389% of its weight in pH 10 buffer. This is the largest degree of absorption observed in these studies for polymers incubated in aqueous media. DI H₂O did not desorb from the film when it was placed in pH 4 buffer to any appreciable degree (Figure 3). However, the pH 10 buffer lost 42.8% of its weight within 15 min before equilibrating at a total weight loss of 76.6%.

Erosion (Degradation) Studies

Polymer matrices with high solvent absorption for long periods of times followed by erosion are good candidates for controlled release formulation of highly soluble drugs.^{17,19,20} Polyesters undergo hydrolytic bond cleavage to form water-soluble degradation products that can dissolve in an aqueous environment, resulting in polymer erosion. In this context, the term “degradation” refers to a chemical phenomenon that involves bond cleavage reactions, whereas “erosion” refers to the physical depletion of material.

Erosion studies have been performed on glycerol-based polyesters made from glycerol and adipic and citric acids degraded by greater than 40% per day in acid or base solutions.³² It was obvious that some of the polymers were eroding as they absorbed DMSO as the material broken into two or more pieces. The films infused with CFG, pectin and sugarcane bagasse, and iminodiacetic had crumbled into pieces by the end of the 24 h trials. The films made from the 2: 1 or 1: 2 molar ratios of glutaric acid to glycerol and the film infused with microcrystalline cellulose were generally intact at the end of the experiment but they would sometimes break into two or three pieces. To determine the amount of degradation occurring for each type of film in water or DMSO, the films were filtered, dried to a constant weight and compared with the original weight of the film. Scanning electron microscopy (SEM) studies show that the topography of the cross sections of the polymer films become smoother with the adsorption and subsequent desorption of water and DMSO (Figure 4).

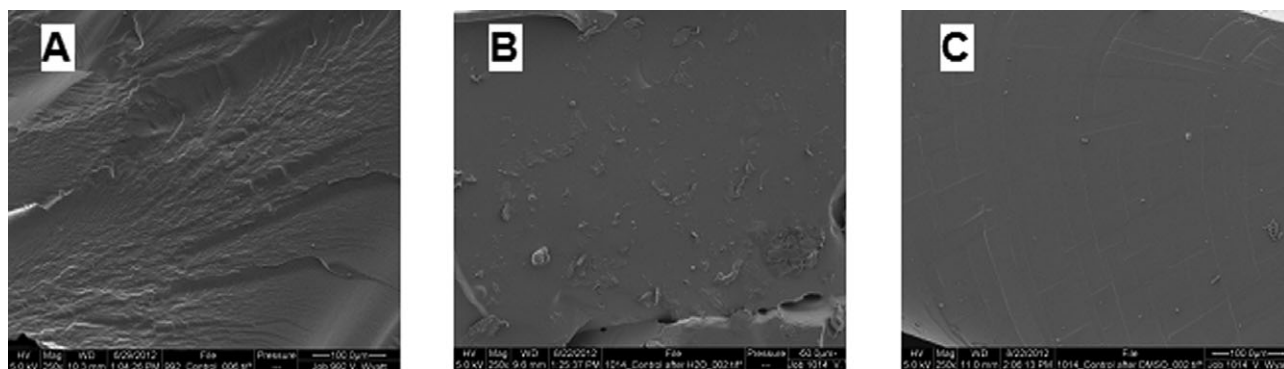


Figure 4. SEM images of (A) 2: 1 glutaric acid: glycerol film before absorbing solvent; (B) after desorption from water; (C) after desorption from DMSO.

In DMSO, erosion ranged from 20.5 to 34.7% for the films infused with the plant cell wall polysaccharides and IDA (Table VI). Erosion was lower (1.9–4.3%) for the 2: 1 and 1: 2 (glutaric acid: glycerol) formulations that were not infused with any additives. In water, erosion for the pectin (32.7%) and IDA (30.3%) were highest. The fact that the percent absorption for the IDA-infused film in water was negative, suggested that erosion for that film was significant in water. CFG (17.6%) also showed significant erosion while the polymer made with sugarcane bagasse, microcrystalline cellulose, and the 2: 1 and 1: 2 (glutaric acid: glycerol) formulations showed percent erosions in the range of 6.3–8.8%. Subsequent erosion studies performed thus far suggest that erosion is insignificant after the second use. The exceptions are polymers infused with iminodiactic acid and pectin that, in time, become gels after they have been incubated in water.

Resorption Studies

Resorption studies were performed on the polymer films that had been recovered after solvent desorption (Table VI). Therefore, resorption studies were performed on the eroded materials and the amounts of solvent resorbed were relative to the weight of the eroded materials. The eroded polymers were more effective solvent absorbers than the original polymer films. While all of the polymers showed an increase in resorption, the polymers infused with pectin (661.8%), CFG (700.0%), and IDA

(740.6%) showed large increases when incubated in DMSO. The IDA-infused film originally absorbed an average of 224% of its weight but it resorbed, on average, 740.6% of its weight. That equates to a 3.3-fold increase in absorption. Resorption of the eroded polymer films in water also showed increases over absorption into the original polymer films. The eroded microcrystalline cellulose polymer resorbed 2.3 times more water than the original film. However, the maximum absorbance of water into eroded materials (51.3%) remained small in comparison to DMSO resorbance.

CONCLUSIONS

This research shows that water absorption can be improved in polymer films made from glycerol and glutaric acid by adding more glycerol or plant cell wall polysaccharides. Absorption in DMSO is maximized after 10 h and can therefore be stopped. Temperature, pH, salt concentration, and combinations of pKa values with solvent polarity affect solvent absorption into the polymer films. Proper understanding of the relationships between these chemical and physical properties and solvent absorption can be used to design stimuli-responsive materials from glycerol. Polymer desorption of adsorbed DMSO and pH 10 buffer into DI Water and pH 4 buffer solutions proved successful. Strong intermolecular interactions between DMSO and water are credited for the observation that DMSO, a solvent readily absorbed into the polymer matrix, cannot be extracted

Table VI. Erosion and Reabsorption Studies

Samples	DMSO			Water		
	% Originally absorbed	% Erosion	% Resorbed ^a	% originally Absorbed	% Erosion	% Resorbed ^a
2: 1 Glutaric acid: glycerol	230.5 (+1.0)	1.9 (±0.2)	271.3 (±17.3)	5.3 (±0.3)	8.3 (±1.5)	6.7 (±1.0)
1: 2 Glutaric acid: glycerol	216.1 (±13.2)	4.3 (±1.3)	304.2 (±13.4)	18.0 (±0.1)	8.8 (±3.6)	18.1 (±2.0)
Corn fiber gum	234.2 (±17.3)	29.4 (±3.7)	700.0 (±40.2)	35.4 (±8.8)	17.6 (±1.7)	51.3 (±4.1)
IDAA	224.0 (±11.2)	34.7 (±3.4)	740.6 (±34.5)	−3.0 (±0.4)	30.3 (±4.3)	0.0 (±0.2)
Microcrystalline cellulose	173.0 (±14.2)	20.5 (±2.3)	227.1 (±9.3)	5.3 (±1.8)	6.9 (±0.7)	12.5 (±1.2)
Pectin	264.5 (±35.3)	23.6 (±0.5)	611.8 (±23.4)	17.5 (±9.9)	32.7 (±3.2)	24.7 (±2.3)
Sugarcane bagasse	171.7 (±0.4)	23.7 (±1.7)	432.4 (±32.2)	7.8 (±2.3)	6.3 (±1.2)	10.0 (±1.7)

^aRelative to weight after erosion.

from water, a solvent that is barely absorbed by the glycerol-glutaric acid polymer films. However, it was shown that DMSO can be extracted from hexane and *t*-butyl acetoacetate. It was shown that 88.2% of the theoretical maximum of DMSO was extracted from hexane. The development of an analytical method for evaluating the solvent before and after extraction of DMSO could be more informative. Erosion and resorption in the presence of DMSO was higher, on average, than erosion and resorption in water. Further investigations are also needed to understand the ability of eroded polymers to absorb larger amounts of solvent than the original polymers. The percent error for some of the repeated trials are higher than desired but those differences can be attributed to the fact that hyper-branched polyesterifications are not controlled reactions and slight variations can exist among the polymers.

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