

# Cellulose/PEO Blends with Enhanced Water Absorption and Retention Functionality

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**ABSTRACT:** This study introduces a novel biodegradable material produced from processing cellulose and regenerating it in aqueous high-molecular-weight polyethylene oxide (PEO). X-ray diffraction and transmission electron microscopic analysis show that the blend is highly amorphous and contains a networked structure of cellulose with packets of PEO encapsulated within the network. Thermal analysis shows that the water loss from the blend is much slower than that from cotton at temperatures above the boiling point of water, which proves enhanced water absorption

and retention properties of the material. It is found that when the material is mixed with sand, up to 1% by weight, the amount of time of water retention in sand increases more than three times. Because of this characteristic, it could be used to improve water storage and availability in sandy soils and to reduce irrigation costs in arid climates. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2121–2127, 2012

**Key words:** biopolymers; differential scanning calorimetry; hydrophilic polymers; renewable resources; blends

## INTRODUCTION

Countries in the Middle East and North Africa are known for the arid climate and sandy soils. These sandy soils have low water retention capability and require large amounts of water for irrigation purposes. Because of the arid climate and the lack of fresh water resources, the water that is used for irrigation is produced mainly through desalination of sea water, which is an expensive process. Materials with good water retention capabilities could be very useful in reducing the water consumed for irrigation purposes. Additionally, they can also stop erosion and water run-off. Polyacrylamides (PAMs) have been extensively investigated as a candidate for an efficient water absorbent for irrigation purposes.<sup>1,2</sup> The slow absorption of water, slow biodegradation, and high cost of PAMs are the challenges faced that limits the wider use of this material in agriculture.<sup>3–6</sup> Additionally, even though polyacrylamides are not toxic, traces of toxic unpolymerized acrylamide can be present in commercially available polyacrylamides which makes it unsafe for use in agriculture.<sup>7</sup> Natural materials such as wood chips and saw dust can be applied as soil amendments to increase the water storage capacity of sandy soils; however, water retention in wood is low.<sup>8</sup> Cheap and biodegradable water-

absorbing polymers could be an answer to address the irrigation challenges in arid climates.

Cellulose is the most abundant biopolymer that can be extracted inexpensively from plants, some animals, fungi, algae, and bacteria.<sup>9,10</sup> More importantly, it is abundantly present in the form of paper waste. Cellulose is known for its hydrophilicity, chirality, broad modifying capacity, and its formation of versatile semi-crystalline fiber morphologies.<sup>11</sup> The biodegradable nature of this inexhaustible biopolymer has encouraged scientists to develop cellulose-based composite materials that can be used as ecofriendly substitutes to existing nonbiodegradable fossil fuel-based counterparts. Modification of native cellulose can change its structure and crystallinity, which essentially determine its physical properties, accessibility to chemical modification, swelling, and adsorption phenomenon. Polysaccharide based superabsorbent materials have also been explored extensively. They are produced mainly through graft polymerization of suitable vinyl monomer(s) on polysaccharide in the presence of a crosslinker or direct cross-linking of polysaccharides.<sup>12,13</sup>

This study introduces a method of modification of native cellulose to produce a novel material with enhanced water absorption and retention properties. The aim of this study is to regenerate cellulose in aqueous PEO so that a renewable, sustainable, and a biodegradable material could be formed that has a higher water absorption and retention capability than native cellulose. It follows a similar modification procedure that is previously reported by our group,<sup>13</sup> in which cellulose is dissolved in 70% sulfuric acid and

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regenerated in ethanol and water. The resulting material from that experiment was regenerated cellulose with a networked structure. However, in this case, dissolved cellulose is regenerated in an aqueous solution of polyethylene oxide (PEO). PEO is a highly hydrophilic polymer that readily dissolves in water and loses its shape. Because of this characteristic, PEO in its normal form would run-off deep below the surface of the soil after a few times of watering. The cellulose/PEO blend reported in this work swells, but does not dissolve in water and thus maintains its physical form. The material is believed to have encapsulated PEO within the networked cellulose that gives it high hydrophilicity when compared with cellulose in its native form. The material is mixed with sandy soils and is characterized for its water absorption and retention properties.

## METHODOLOGY

### Fabrication

#### Materials

Microcrystalline cellulose (MCC;  $M_w = 350,000$ ) was purchased from FMC Biopolymer (Philadelphia/Pennsylvania), and sulfuric acid (99.9%) and PEO ( $M_w = 4,000,000$ ) were purchased from Sigma-Aldrich (St. Louis/Missouri). Sulfuric acid was diluted to a concentration of 70% (w/w).

#### Acid hydrolysis of MCC

Acid hydrolysis is performed in a Varian dissolution system in which the water bath is adjusted to 5°C. Sulfuric acid of 70% concentration is added to a vessel and is stabilized to reach 5°C. Subsequently, 20 g of MCC is added to 200 mL sulfuric acid, and the resulting solution is mixed for 30 min at 5°C at 250 revolutions per minute to form Solution A. The formed mixture is a viscous and transparent liquid of cellulose completely dissolved in sulfuric acid.

#### Regeneration of cellulose

Solution B was prepared by dissolving PEO in deionized (DI) water. PEO was dissolved in DI water and heated at 50°C for 14 h at 500 rpm and then left to cool to room temperature. About 1 g of PEO is used for every 4 g of MCC dissolved in sulfuric acid. In this experiment, 5 g of PEO was dissolved in 200 g of (distilled) water is used to dissolve 5 g of PEO to achieve a aqueous PEO solution with a concentration of 2.5% (wt./wt.). The water acts as a solvent. Since we used 20 g of MCC, 5 g of PEO was used for the regeneration process. The resulting volume of aqueous PEO solution was 200 mL. Following the mixing of MCC in sulfuric acid for 30 min at 5°C, PEO solu-



**Figure 1** Picture of hydrated GELPEO lumps after dialysis. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tion (Solution B) is added as a precipitating agent to the Solution A. The resulting material is left to mix at 5°C and 250 rpm for 30 min.

The concentration of sulfuric acid drops to 35% after regeneration. After the regeneration of cellulose using PEO solution, the resulting material is immediately centrifuged at 4°C and 2400 rpm to remove sulfuric acid and excess PEO. Because of the low temperature, low concentration of sulfuric acid, and shortage of time, it is believed that the PEO does not degrade. The centrifugation process resulted in separating the precipitated material from the spent liquor. The precipitate was collected again and dialyzed (against running tap water) for 3 days until the pH of the suspension reached 6–7. The resulting material predominantly consisted of small hydrated gel-like lumps (Fig. 1), which will be referred to as GELPEO from now onward.

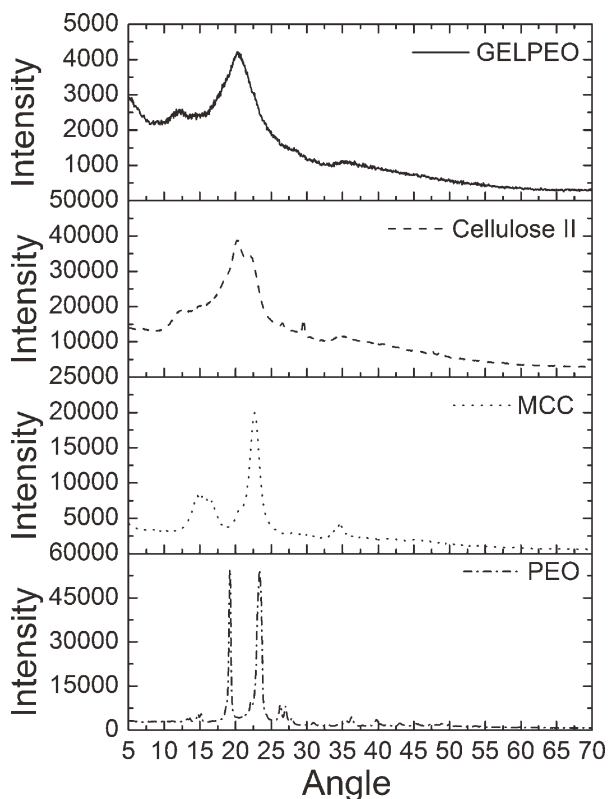
### Characterization

#### X-ray diffraction

X-ray diffractograms of the samples of oven-dried GELPEO, PEO ( $M_w = 4,000,000$ ) powder, and MCC ( $M_w = 350,000$ ) were obtained on an X-ray diffractometer (PANalytical, X'Pert Pro). Samples of GELPEO were prepared by air drying the GELPEO suspension on Quantifoil® grids (SPI).

#### Transmission electron microscopy

The sample for transmission electron microscopy (TEM) was prepared using Focused ion beam (FIB) lamella lift out and thinning method. First of all, a layer of chromium was deposited on the surface of the sample to get a SEM image of the sample while doing FIB milling. Then, a protection layer of silicon and platinum was made to protect the structure of the GELPEO while milling with ion beam.



**Figure 2** X-ray diffractogram of GELPEO, cellulose II, MCC, and PEO.

A lamella of  $3 \times 20 \times 3 \mu\text{m}^3$  was lift out using a microprobe and was then thinned down to a thickness of only 150 nm, which is sufficient for polymer materials to give atomic resolution in TEM. The images attached

are bright field images produced by using a low-intensity beam to minimize artifacts induced by the beam.

#### Differential scanning calorimetry

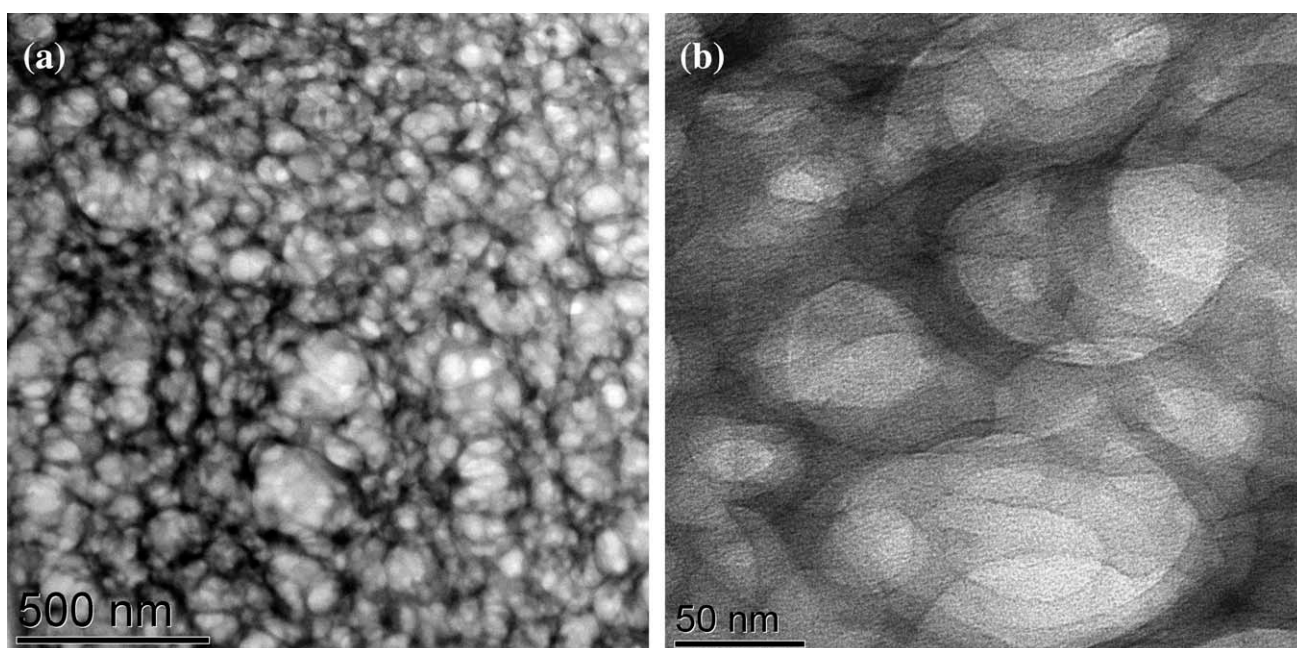
Differential scanning calorimetry (DSC) studies were carried out on a DSC4000 (Perkin-Elmer) machine. Excess water is added to GELPEO, cotton, and sandy soil and left for 5 h to allow the materials to absorb materials to the point of saturation. The samples with excess water were collected and heated from 20 to 200°C at a heating rate of 1°C/min under a nitrogen flow of 20 mL/min.

#### Thermogravimetric analysis

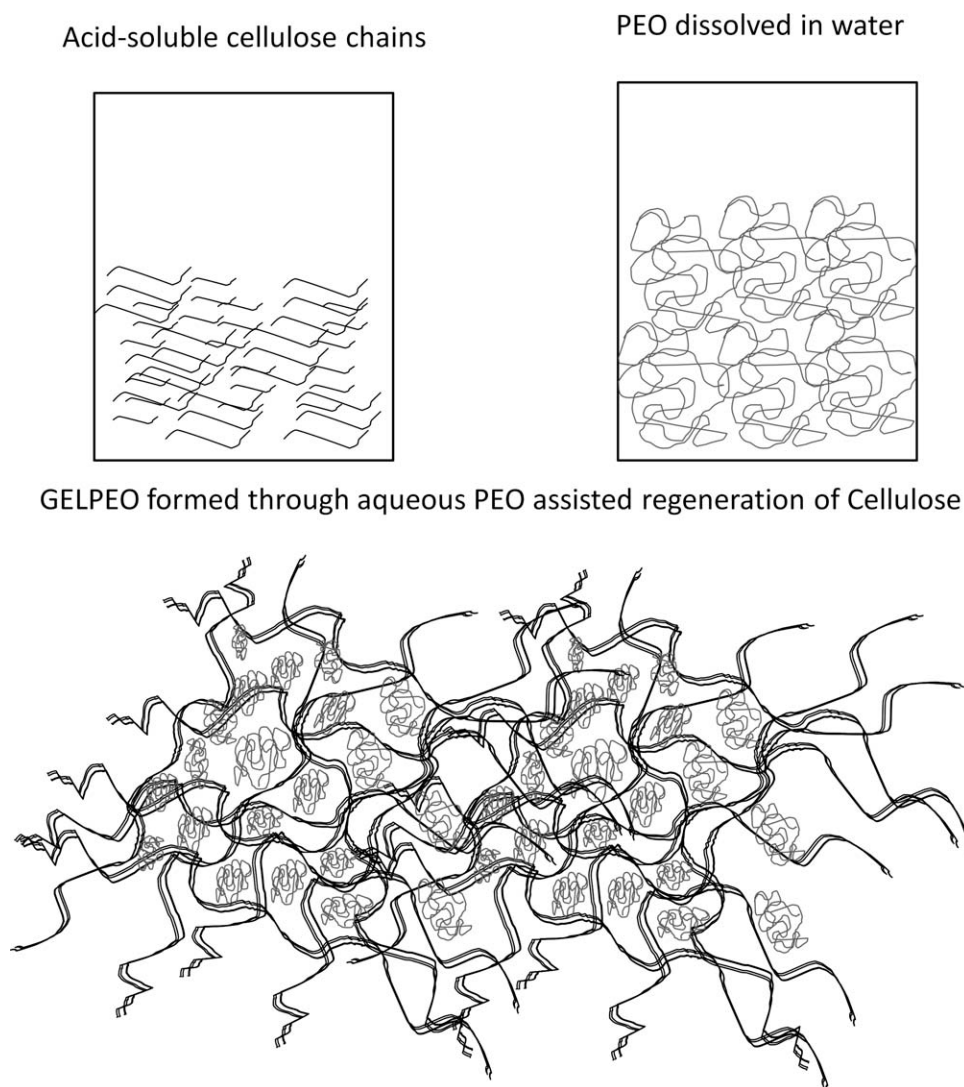
The thermogravimetric analysis (TGA) study was done on a TGA6000 (Perkin-Elmer) machine. The hydrated samples of GELPEO, cotton, and sandy soil were placed in the TGA crucible and heated from 20 to 250°C at a heating rate of 5°C/min under a nitrogen flow of 20 mL/min.

#### Water absorption

Water absorption of the different samples of materials was measured by first immersing all the samples in water for 5 h to allow the materials to absorb water to the point of saturation. The water-saturated samples were then sieved for 1 min to drain excess water and then left to dry. The weight of the hydrated sample was taken before and after drying to measure the amount of water absorbed by each sample.



**Figure 3** TEM images of GELPEO (a and b) showing networked dark regions (cellulose) and packets of encapsulated lighter regions (PEO).



**Figure 4** Schematic of GELPEO formed through aqueous PEO-assisted regeneration of cellulose.

#### Outdoor testing

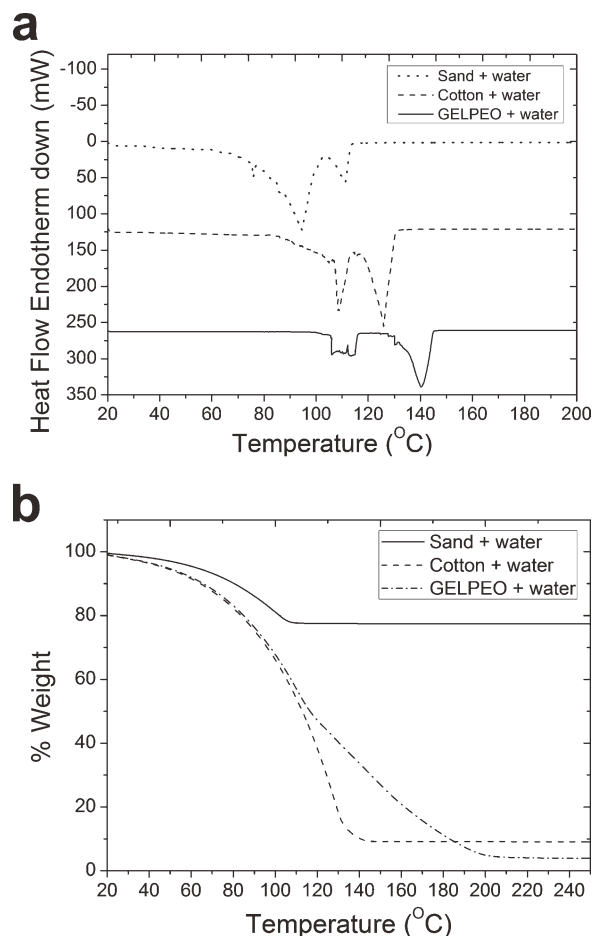
Samples of mixtures of sandy soil with weight proportions 0, 0.33, 0.67, and 1% dry GELPEO are prepared. As a reference, mixtures of sandy soil with weight proportions of 1% cotton, 1% wood chips, and 1% saw dust are also prepared. All the samples are placed in small pots with drain holes and watered with the same weight of DI water. The water was allowed to drain, and the pots were placed outside under direct sunlight. Water absorption and retention over time is measured.

## RESULTS AND DISCUSSION

### X-ray diffraction and transmission electron microscopy

X-ray diffraction (XRD) patterns of oven-dried GELPEO revealed that the material is highly amorphous when compared with the starting materials MCC

and PEO powders. Figure 2 shows that the characteristic peaks of MCC and semicrystalline PEO are not present in the diffractogram for GELPEO. Alternatively, it can be seen from Figure 2 that the GELPEO adopts a structure very similar to that of cellulose II. When PEO is dissolved in water and when cellulose is dissolved in concentrated acid, the PEO chains randomly arrange themselves while the layers of cellulose chains are attacked by the acid and are opened up. Subsequently, when the aqueous PEO is added to acid-dissolved cellulose, the cellulose regenerates immediately and gives very little time for cellulose and PEO to arrange itself in some kind of order. Consequently, the cellulose chains partially recrystallize to a more stable networked cellulose II structure, whereas the aqueous PEO becomes trapped within the network in this process. Therefore, PEO that is present in this blend is highly amorphous in nature, and thus the X-ray diffractogram of GELPEO shows no semicrystalline peaks of PEO.



**Figure 5** DSC curve (a) and thermogravimetric analysis (b) for samples of hydrated sand, cotton, and GELPEO.

TEM images [Fig. 3(a,b)] of GELPEO confirm the networked structure of cellulose with packets of PEO encapsulated within the networked cellulose. A similar networked structure of cellulose has been obtained earlier by our group through the exact same processing but with regeneration in water.<sup>14</sup> The combination of XRD and TEM images obtained suggest that the dark areas in the TEM images show networked cellulose that has some sort of order, whereas the lighter areas represent the highly amorphous PEO that is encapsulated within the networked structure of cellulose. A schematic of the structure of GELPEO formed through aqueous PEO-assisted regeneration of acid-soluble cellulose is shown in Figure 4. The high-molecular-weight and hydrophilic PEO that is encapsulated within the networked cellulose is believed to give the material a gel like physical appearance.

#### Differential scanning calorimetry and thermogravimetric analysis

Figure 5(a) shows the DSC curves obtained for samples of sand, cotton, and GELPEO with excess water. The DSC curves obtained for the three samples each

showed two endothermic peaks. One peak at around 110°C is common between all the three samples, and this corresponds to the phase change of the unabsorbed or free water in the sample. The other peak is identified as the thermal energy needed to separate the absorbed water from the surface of the specific material being tested. Water that is absorbed by sand is released at a relatively low temperature of 90°C, whereas water is retained in cotton and GELPEO up to 125 and 140°C, respectively. The high water retention by GELPEO shows that GELPEO is capable of storing water for longer times at higher temperatures.

TGA [Fig. 5(b)] corroborates the behavior observed by the DSC. When the hydrated samples of sand, cotton, and GELPEO are heated, the evaporation of water takes place at different rates. The slowest rate of weight loss occurred in the sand sample as the amount of water absorbed in the sand sample was very small. The evaporation rate of water occurs at the same rate in the cotton and GELPEO sample up to the boiling point of water as identified by the DSC. The rate of water loss after that slows down considerably for the GELPEO sample, as it is believed that there are strong forces between water molecules and the GELPEO surface which gives it the hydrophilic nature. This allows GELPEO to absorb and retain more water when compared with cotton.

#### Water absorption

Water absorption was measured for samples of sand, cotton, GELPEO, wood chips, and saw dust. From the results, it was found that the hydrated sample of sand contained only 20% water, whereas the hydrated cotton and hydrated GELPEO samples contained 90 and 95% water by weight, respectively. This is also corroborated by the TGA performed on hydrated samples of sand, cotton, and GELPEO in Figure 5(b). Hydrated samples of traditional organic materials such as wood chips and saw dust contained 70 and 89% water. Water content of 95% by weight in the GELPEO sample is significantly higher than the water content found in the other samples and signifies that GELPEO is capable of absorbing water up to 20 times its own weight.

#### Outdoor testing

The outdoor testing clearly demonstrated the effect of adding small percentages of GELPEO in sand. First, draining of the tested samples revealed that most of the water escaped from the neat sand sample. The samples with increasing weight percentages of GELPEO managed to absorb more water and thus had higher weights after water draining. Within the first hour, a major difference was noted between the samples with 0, 0.5, and 1% GELPEO in sand. The

**TABLE I**  
**Experimental Results of Sand Samples with Different Percentages of GELPEO and Cotton**

Sample	Day temperature (°C)	Night temperature (°C)	Weight without water (g)	Weight after water added (g)	Weight after excess water drained (g)	Time to evaporate all water (h)
Sand			150	232.8	218.1	50
Sand + 0.33% GELPEO	Max.: 43.5	Max.: 35.6	150	232.8	230.4	99
Sand + 0.67% GELPEO	Avg.: 37.1	Avg.: 30.0	150	232.8	229.5	123
Sand + 1% GELPEO	Min.: 26.8	Min.: 24.0	150	232.8	230.7	149
Sand + 1% Cotton			150	232.8	231.4	73

neat sand sample lost water very quickly. It took 45 h for the sample with 1% GELPEO to lose the amount of water that the neat sand sample had lost in 1 h. The sample with 1% cotton lost water at a slower rate when compared with the sample with the neat sand but at almost double the rate as the sample with 1% GELPEO. It can also be seen that the rate of decrease of water over the first 24 h was much less for the samples with small percentages of GELPEO. Table I shows the weights of the drained samples and the time taken to evaporate all the water from the tested samples.

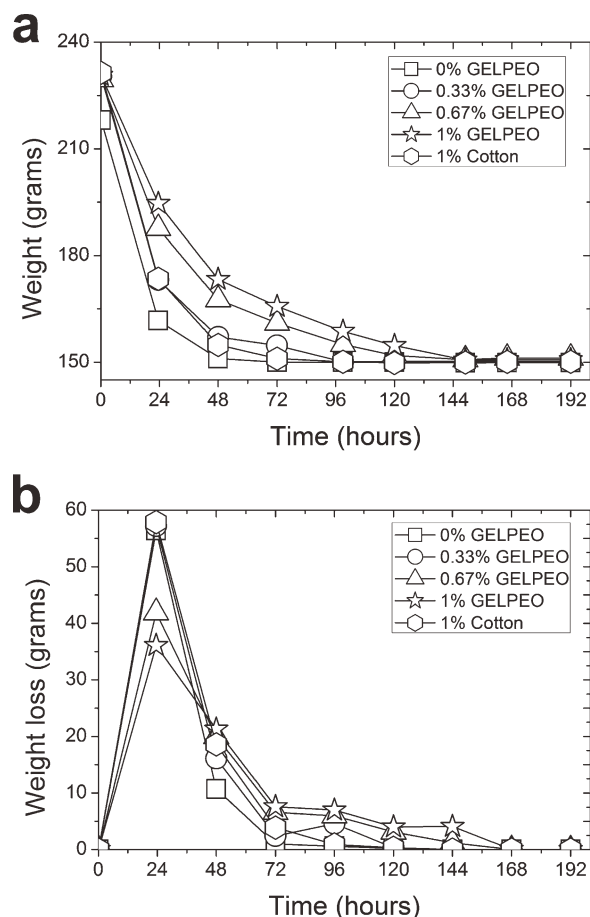
Figure 6(a,b) shows the decrease in the weight of GELPEO over time under outdoor testing after draining of water. From Figure 6, it can be seen that the evaporation rate of water in the different samples varied according to the amount of GELPEO added. As the percentage of GELPEO in the sample increases, the water retention capability of the sample also increases. The outdoor tests were performed in the mid of June, which is representative of summer weather in Abu Dhabi. The maximum, average, and minimum day and night temperature recorded during the period of testing is given in Table I. Figure 6(b) shows the loss of water against time. Samples with GELPEO retain more than half of the water content over the first 24 h, whereas samples with 1% cotton and 0% GELPEO lose most of its water content in the first 24 h.

## CONCLUSIONS

A novel functional material is developed that is based on cellulose and PEO. The material is mainly amorphous with cellulose being regenerated partially in cellulose II structure. TEM images revealed a networked structure of cellulose with packets of PEO encapsulated within the network. Because of the fast regeneration process, little time is allowed for PEO or cellulose to arrange itself, and thus both exist in mostly amorphous forms in the blend. The material is capable of retaining water above the boiling point of water and that the water loss from the material is slower than that from cotton. It is found that GELPEO is capable of holding water 20 times its own

weight, whereas neat sand and other organic soil amendments such as wood chips and saw dust have poor water absorption properties. Because of these characteristics, the water run-off during irrigation could be reduced and water could be conserved.

Furthermore, it is found from the outdoor testing that the addition of 1% GELPEO in sand could significantly increase the absorption and retention of water. With the addition of 1% GELPEO in sand, water could be retained for more than three times longer under the same environmental conditions. The development of this material can be significant in decreasing the frequency of irrigation, which



**Figure 6** (a) Weight and (b) weight loss of wet sand samples with different weight percentages of GELPEO and cotton over time during outdoor testing.

would contribute to the lowering of water consumption in arid climates. The enhanced water retention ensures that crops grown would have much better availability of water and could thus grow at a faster rate than normal. As this material is based on cellulose, its use would be environmentally friendly unlike current commercial PAM-based materials.

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