On the Assessment of Hydrogels for Fluid Absorbency

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SYNOPSIS

Hydrogels are capable of absorbing fluids like water to the extent of several fold. Since this is an important characteristic property of any hydrogel, it is necessary to employ a simple and accurate method for its assessment. Several methods reported in the literature have been discussed for their scope as well as limitations. A comprehensive approach on the basis of polymer structure–property application is made to evaluate suitable methodology for two types of hydrogels, continuous and discrete. Representative methods for both type are suggested with detailed experimental procedures and results. The work provides comparative data with suggested methods which could be useful to the practitioner. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels are water-swollen hydrophilic materials.[1] Such materials may be inorganic or organic and natural or synthetic. In a fluid like water, they swell to an equilibrium extent preserving their shape. The stability of the shape is primarily due to the presence of three-dimensional partially crosslinked network structure and the hydrophilicity due to the presence of water-solubilizing polar groups along the polymer.[2]

The equilibrium swelling results usually from a balance between dispersive (repulsive) and cohesive (attractive) forces acting simultaneously in the fluid. Factors affecting the swelling of hydrogels are listed in Table I.

When a hydrogel is mixed in a fluid it undergoes simultaneous swelling, absorbing the fluid in a kinetic manner. At equilibrium, it is no longer capable of absorbing more fluid. The quantity of fluid at the equilibrium is referred to as fluid uptake or absorbency and usually described as a bulk quantity in grams (of fluid) per gram (of the hydrogel). Since this is an important property which describes the efficiency and possible applications of the hydrogel,

its precise assessment is essential. This paper reports classification of hydrogels with respect to various methods including their merits and limitations.

A few commercially available hydrogels were also tested using respective methods with a view to establish the validity of the methods.

EXPERIMENTAL

Materials

Double-distilled water was used in preparing the polymer solutions. Sodium chloride (NaCl) and sodium hydroxide (NaOH) were of analytical reagent grade from E. Merck. The acrylic type hydrogel (designated as polymer I) was typically a partially crosslinked poly(methacrylic acid), partially esterified as well as neutralized with the alkali to yield pH 7.0. The starch type hydrogel (designated as polymer II) was typically a hydrolyzed starch polyacrylonitrile graft copolymer sodium salt. Both the polymers were obtained from the GSFC Research Centre and used in the study without further purification. The hydrogels passed through a 500-μm sieve were preequilibrated in a desiccator in order to have a uniform residual moisture content of 10%, which otherwise could lead to erroneous water absorptions. All materials were weighed to 0.1 mg accuracy.

Table I Factors Affecting Hydrogel Swelling[3]

Increase Swelling	Decrease Swelling
Dispersing forces	Cohesive forces
Hydrophilic groups and moieties	Hydrophobic groups and moieties
Low crosslinking density	High crosslinking density
High chain flexibility	Low chain flexibility
High free volume	Low free volume
Osmotic potential	Dipole–dipole interaction
Electrostatic repulsion	Impurities in the fluid

A few commercial hydrogel products employed in the study are listed in Table II. Since it is intended to evaluate the validity of test procedures and not the validity of commercial products, the results are expressed on arbitrary designations.

Methods

Swelling Value

This is also referred to as the pyknometer method in which a 25- or 50-mL capacity specific gravity bottle is employed. The specific gravity of dry and swollen polymer is evaluated against paraffin oil (specific gravity = 0.8148) at 25°C. The values are then normalized against that of water (specific gravity = 1.000) and converted into respective volumes. The extent of swelling is calculated on the basis of the percentage of relative difference.

Water Retention Value (WRV)

This is also referred to as the centrifuge method in which the amount of water retained by the swollen hydrogel is determined after applying a centrifugal force over a definite period of time.[4] A known quantity of hydrogel is dispersed in water and centrifuged
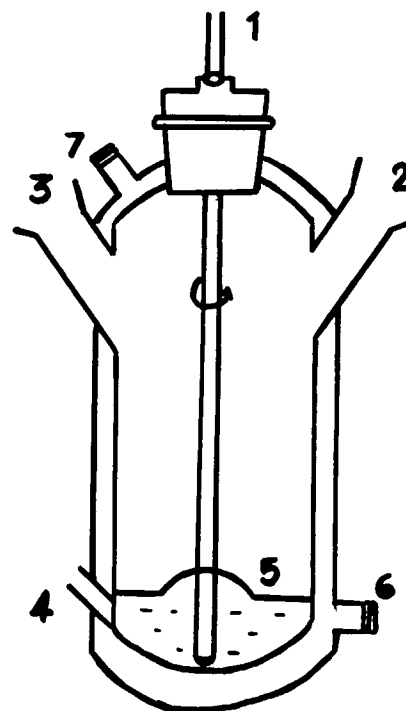

Figure 1 Schematic diagram of glass apparatus for assessment of fluid absorbency of a hydrogel based on vortex principle. 1, glass rod through Teflon pulley; 2, side arm with B-14 socket for condensor; 3, side arm with B-14 socket for pressure equalizing glass funnel; 4, thermometer pocket; 5, a typical upward vortex under stirring; 6, water inlet; 7, water outlet.

at 25°C for 0–60 min between 1000 and 15000 rpm. A fixed angle rotor centrifuge (Model Beckman JA18 from Beckman Inc., USA), equipped with fine mesh strainers, is used for the purpose. The amount of water retained under the dynamic equilibrium condition is calculated on the basis of the relative weight difference.

Vortex Method

A glass apparatus as shown in Figure 1 is clamped vertically and the hydrogel solution is equilibrated

Table II List of Commerical Hydrogels Employed in the Study

| Trade Name	Chemical Description[a]	Origin
Waterlock, B-204	Hydrolyzed-starch-g-polyacrylonitrile alkali salt	Grain Processing Corportion, USA
Waterlock, G-404	Poly(acrylamide-co-acrylonitrile)	Grain Processing Corporation, USA
Superslurper	Hydrolyzed starch-g-polyacrylonitrile	Superabsorbent Company Inc., USA
Supersorb-F	Copolymer acrylamide-acrylate	Aquatrols, Inc., USA
Supersorb-C	Crosslinked polyacrylamide copolymer	Aquatrols, Inc., USA
Jalshakti	Starch-based absorbent polymer	Indian Organic Chemicals Ltd., India

[a] Based on Company's Literature.
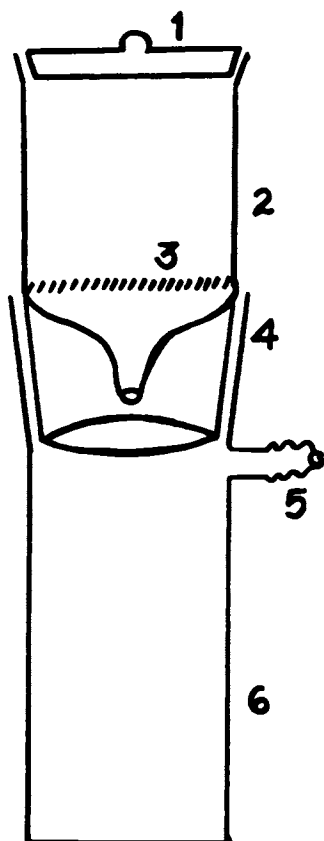
Figure 2 Schematic diagram of glass apparatus for assessment of fluid absorbency of a hydrogel by the modified crucible method. 1, ground glass lid; 2, crucible with 50 mL capacity; 3, a G-4 sintered ceramic disc; 4, a B-34 standard joint; 5, nozzel for vacuum; 6, reservoir.

to a constant temperature. Then the glass rod is stirred at high speed with an electric motor (typically 1000 rpm) so as to observe an upward vortex. Subsequently, the fluid is added dropwise through the side arm under continuous stirring until the vortex disappears and the liquid surface becomes flat. A lamp can be focused to illuminate the surface. The total quantity of fluid per gram of polymer is calculated and reported.

Crucible Method[5]

A glass apparatus as shown in Figure 2 is clamped vertically. A sample of hydrogel solution is taken in the crucible (modified Gooch crucible with sintered ceramic disc, grade G4 signifying average pore diameter of 10 μm). The excess fluid is removed by applying a partial vacuum through the nozzel. The total quantity of fluid per gram of polymer is calculated from the weight difference. The lid is replaced to minimize water evaporation when there is no vacuum applied.

RESULTS AND DISCUSSION

The basic significance of the hydrogel lies in its capacity of suction, retention, and gelation with fluid to help develop polymer structure–property relationships. Its practical significance lies in its subsequent applications based on the particular methodology employed as described in Table III.

Before going into details of these methods, it is necessary to understand the solution behaviors of the hydrogels. Holly and Refojo,[6] based upon high contact angle hysteresis with water, reported that the gel interface is capable of changing its polarity through conformational and orientational changes of its polymeric chains depending upon the polarity of the adjacent liquid phase. Depending upon chain rigidity or flexibility and the size of macromolecular aggregates, it is proposed to classify hydrogels into two groups, continuous and discrete (dispersed with respect to the fluid phase). The acrylic hydrogel is a typical example of the continuous type and the starch hydrogel is a typical example of the discrete type. In our view, this clarification is required since many methods are applicable to only one type of hydrogel.

In the filtration method, the hydrogel is swollen in an excess of water and the excess water is filtered through a screen. The limitation of this method especially with the continuous type hydrogels is that the excess water is not that easily filtered and perhaps the interface in immediate contact with the screen loses more water. In the case of discrete type hydrogels, this method does work satisfactorily since the excess water gets removed through internal "channels" of swollen hydrogel globules.

In the vortex method, a fixed volume of liquid is poured in a beaker, the polymer is introduced while stirring, and time required for the vortex to disappear is measured to assess the gelation power. However, in case of some hydrogels the disappearance of the vortex may take extremely long time, making

Table III   Methods for Assessing Water Absorbing Power of Hydrogels[13]

Function	Methods
Suction power	Capillary method
Retention power	Filtration method
	Tea-bag method
	Sheet method
	Centrifugal method
Gelation power	Vortex method
	Flow method

the method unsuitable in such cases. Similarly, in the flow method, the polymer is placed in a beaker, the liquid is added to make it swell, and the point at which the gel starts to flow indicates the end point. This is also known as the beaker method. This does not account for gel/glass interactions since both have definite polarity. Both these methods may not be applicable to discrete gel systems.

In the tea-bag method, the hydrogel is enclosed in a nonwoven bag, dipped in fluid for a certain time period, and weighed after draining water. The limitation with this method is that the nonwoven bag may absorb a portion of the fluid through capillary action and it may be difficult to obtain a constant weight after draining. Though this method is applicable to both types of hydrogels, all hydrogels may not respond to swell quickly, requiring longer dipping time, and some may not get fully swollen without some mechanical action like stirring in the initial stage.

In the blot-weigh method[7,8] a predried and weighed sample of hydrogel is placed in a fluid reservoir and allowed to swell to equilibrium. Afterward, the excess water is removed from the hydrogel by blotting with a tissue or a filter paper and weighed to compute the difference as a measure of fluid absorbency. Wiping the gel surface with a tissue may be a source of error since this may leave either tissue fibers on the gel or gel on tissue fibers.

Alhaique and co-workers[9] have reported a method wherein the polymer is allowed to swell in a graduated cylinder and the volume change is noted. There are two apparent limitations. First, it could be difficult to differenciate the gel/fluid interface since the fluid is usually in excess. Second, most of the swollen gels do not yield a uniform top surface producing errors in volume measurements. Other researchers[10] have used vernier callipers to measure the swollen volume of the gel. Hydrogels are usually soft and pliable materials and hence fine adjustment by a vernier screw may sometimes deform the surface leading to errors.

The swelling of hydrogels has been reportedly monitored by the use of optical microscopy,[11,12] phase transfer light microscopy,[13] as well as laser the diffusion technique.[14] These methods provide good means of studying the kinetics of swelling and swollen volumes by video photography, but they require sophisticated instruments and trained personnel involving high cost of assessments.

Water absorption data by the tea-bag method, typical of both the hydrogel types (I = continuous, II = discreet) are given in Table IV. A large deviation

Table IV   Water Absorption Data of Both Types of Hydrogel Polymers by the Tea-Bag Method

Hydrogel Polymer Type	Replicate Sample No.	Amount of Water Absorbed (g/g)	Deviation from Average Value
I	1	180.71	−39.42
	2	197.20	−22.93
	3	297.00	+76.87
	4	246.52	+26.39
	5	179.22	−40.91
II	1	446.20	+46.05
	2	424.12	+23.97
	3	341.94	−58.21
	4	378.33	−21.82
	5	410.15	+10.00

of values is observed in both cases, questioning the suitability of the method.

Water Retention Values (WRV)

This may be viewed as a water-holding capacity of the hydrogel under dynamic equilibrium conditions. This is accomplished in a laboratory centrifuge at a relatively higher speed of rotation. In order to eliminate the geometric variation of the instrument rotor, the results were computed in terms of relative centrifugal field (RCF). This is, in principle, the ratio of the centrifugal acceleration at a specified radius and speed (rw^2) to the standard acceleration of gravity (g) according to the following formula[15]:

$$RCF = \frac{rw^2}{g}$$

where r is the radius in millimeters, w is the angular velocity in radians per second (2 Π rpm/60), and g is the standard acceleration of gravity (9807 mm/s^2).

WRV of acrylic polymer as a function of RCF with respect to polymer concentration is depicted in Figure 3. It is evident that WRV remains constant with increasing RCF, except at 10 units the value is decreased irrespective of the polymer concentration.

This phenomenon may be attributed to the removal of "free" water (not bound directly with the macromolecule) and, because of this, the polymer with lower concentration loses larger water at a faster rate compared to polymers at higher concentrations. In other words, the value of 10 RCF is the energy sufficient to detach the free water from the hydrogel polymer under consideration.
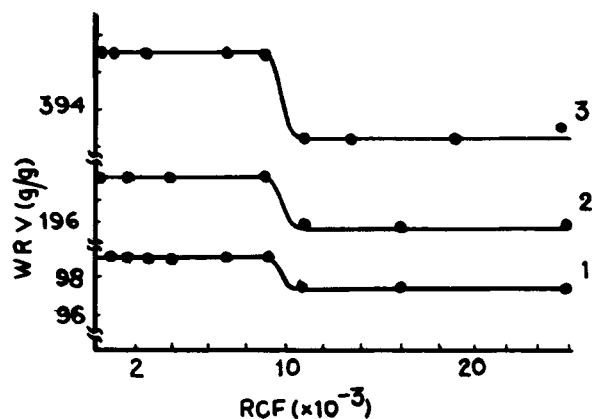
Figure 3 Water retention value (WRV) of hydrogel (polymer type I) as a function of relative centrifugal force (RCF) for various polymer concentrations. 1, 1%; 2, 0.5%; 3, 0.25% w/w at 25°C.

Swelling Value

Swelling of hydrogel can be expressed in weight, volume, and length units at equilibrium conditions. The weight percent of water in a hydrogel is

$$W = 100 \, (\text{wet weight} - \text{dry weight}) / (\text{wet weight})$$

Swelling related to the dry state is referred to as hydration, water regain, or swelling value expressed as

$$S = 100 \, (\text{wet weight} - \text{dry weight}) / (\text{dry weight})$$

Since the specific gravity of water is unity, for practical purposes the above equation can be considered as

$$S = 100 \, (\text{wet volume} - \text{dry volume}) / (\text{dry volume})$$

The swelling of the acrylic type hydrogel as a function of hydrogel concentration is shown in Figure 4. The swelling decreases as a function of hydrogel concentration in a curvillinear manner. This indicates a faster decrease at lower concentrations and slower decrease at higher concentrations. This also indicates that it is necessary to fix the quantity of dry hydrogels, say 1 or 0.1 g, for the purpose of their relative comparisons.

An attempt has been made to compare swelling and water retention value of various concentrations of acrylic type hydrogel. The data given in Table V indicate that both values are nearer and any method can be followed for the type of hydrogel under consideration. These methods are somewhat tedious and time consuming.
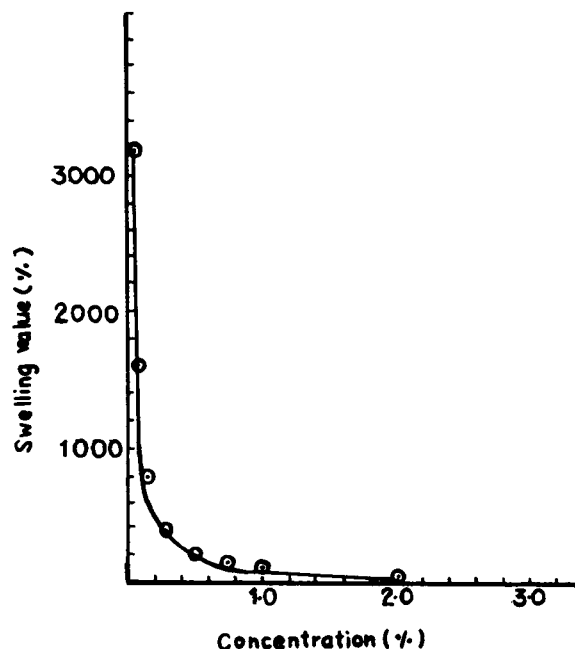

Figure 4 Swelling value of hydrogel (polymer type I) as a function of hydrogel concentration using a pyknometer at 25°C.

Vortex Method

A simpler method suitable for polymers of type I is described in Figure 1. These types of polymers have a common tendency to flow upward around the rotating glass rod making a convex vortex. Upon dilution, the convex vortex decreases and becomes flat. This is considered as the end point. The reason may be attributed to the gradual change of interface from glass/polymer rich to glass/fluid rich with corresponding flattening since a fluid like water does not give an upward vortex. Typical data obtained with this method are given in Table VI. It becomes essential to alter the fluid, for example, urine for diaper application. Dilute salt solutions can also be employed to represent such fluids. Typ-

Table V   Comparison of Swelling and Water Retention Values for Acrylic Type Hydrogel at Various Concentrations

Hydrogel Concentration (%)	Swelling (%)	Water Retention Value (%)
1.00	95.12	97.31
0.75	133.41	135.18
0.50	200.33	197.58
0.25	399.15	392.36

Table VI   Water Absorption Data by the Vortex Method (Polymer = type I)

Media	Amount of Fluid Absorbed (g/g)
Pure water	202.41
NaCl soln., 0.4%	81.95
NaCl soln., 1%	62.73

ical data with sodium chloride solutions are illustrated in Table VI.

This method is relatively quicker and facilitates water absorption as a function of temperature also. This is particularly useful in acrylamide type gels which also function upon temperature. Moreover, the polymer can be precipitated *in situ*, dried under vacuum, and tested for repeated fluid absorbency. This is required for assessing hydrogels for successive swelling and drying cycles in simulating field application data.

Crucible Method

In this method, a small amount of dry hydrogel is placed in a sintered glass crucible followed by water. The ground glass lid is closed and the crucible is allowed to stand overnight with occasional shaking of the mass. Afterward, the lid is removed and a partial vacuum from the bottom side is applied to remove excess water from the swollen mass of the hydrogel. In order to decide optimum time of vacuuming, the acrylic type hydrogel was assessed at three levels of concentrations for long interval of time. The results shown in Figure 5 indicate that water gets continuously removed from the hydrogel in a linear manner. The rate of water removal (slope of straight line) is inversely proportional to the hydrogel concentration, which is obvious in view of hydrogel–water interactions. For a concentration of 0.5%, when the material is repeatedly assessed, there is no significant change in water removal. However, after drying and redispersing the hydrogel, it is found that both water uptake and removal are significantly changed. Since this method does not reach equilibrium, it may not be considered suitable for continuous types of hydrogels.

When the same method is applied to discrete type of hydrogels, relatively quick equilibriums are observed when the hydrogel no longer gives off a significant quantity of water. Typical data are given in Table VII with the possibility of employing salt solutions. It may be suggested that both time of vac-
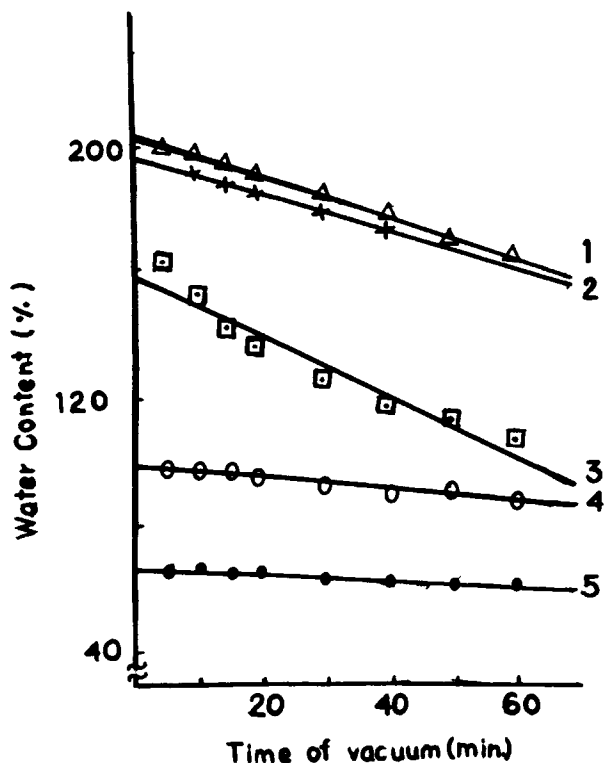

Figure 5 Water content of hydrogel (polymer type I) as a function of vacuum time. 1, 0.5% concentration; 2, 0.5% repeat; 3, 0.5% repeat after drying the hydrogel; 4, 1.0%; 5, 1.5% w/w at 25°C.

uuming and flow of vacuuming should be standardized for future adoption of this method.

With a view to assessing the suitability of the method for commercial hydrogel products, six internationally available products were evaluated. The

Table VII   Water Absorption Data by the Crucible Method (Polymer = type II)

Media	Time of Vacuum (s)	Pure Water Flux, (mL/s/cm^2)	Corresponding Amount of Fluid Absorbed (g/g)
Pure water	0	0.0	300.00
Pure water	10	0.07	271.25
Pure water	15	0.07	250.19
Pure water	30	0.07	249.74
Pure water	60	0.07	248.92
Pure water	15	0.05	253.87
Pure water	15	0.09	248.61
NaCl soln., 0.4%	15	0.07	110.15
NaCl soln., 1%	15	0.07	79.63

Table VIII Relative Assessment of Water Absorption by Commercial Hydrogel Products

Arbitrary Product No.	Water Absorption (g/g)
1	180.3
2	950.5
3	150.8
4	330.3
5	397.0
6	206.4

results obtained are depicted in Table VIII, which substantiates the method.

This method is simple and accurate. Moreover, repeated swelling and drying cycles of the polymer can also be studied as the polymer mass can be conserved accurately.

Note: It may be better to discuss three important matters, in general:

1. Prolonged vacuuming of the gel in a crucible will give "air-cracks" in the gel if it is of the discrete type, giving a clue for the qualitative purpose.
2. For comparison of various dry gel powdery samples, samples should be equilibrated to a constant residual water content (say 10 or 15%), otherwise water absorbency results may lead to different values.
3. The data with salt solutions are useful in interpreting the gel's efficiency in saline water or in urine.

CONCLUSIONS

The most important property for a hydrogel is its ability to absorb a fluid like water. It is necessary to evolve a simple and accurate method for assessment of fluid absorbency of the hydrogel. The hydrogels are classified as continuous or discrete depending upon their physical interaction with the fluid. Many methods reported in the literature have limitations and result in improper assessments. For the continuous type hydrogels, the vortex method is found suitable and for the discrete type hydrogels, the crucible method is found suitable. With the vortex method reported, it is possible to assess fluid uptake as a function of temperature also. The method is found suitable for evaluation of a few representative commercially available hydrogel prod-

ucts. Any one single method is not applicable to all types of hydrogels.

The paper considers applied aspects of hydrogel polymers and presents a comparative study for evaluating the swelling characteristics of hydrogels and suggests guidelines which would be useful to the practitioner. It may be further stated that there are no universally accepted test procedures or applicable ASTM/ISO methods for measuring hydrogel absorbency. Therefore, the methods illustrated in this paper may be subject to reformulation, interlaboratory cross-checking, and adoption by bodies like ASTM/ISO.

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