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Hydrophilicity of 3-D biomaterials: The Washburn equation

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Characterisation and quantification of the surface energy of biomaterials used as tissue engineering scaffolds is important, but many of the techniques available to examine these properties are only applicable to smooth flat samples, not porous materials. This paper describes the application of the Washburn equation to measure the surface energy of a range of porous polyether polyurethane scaffolds with three test liquids; *n*-Hexane was used to measure a material constant, whilst ethanol and xylene were used to measure contact angles. The results show that the Washburn equation is not applicable in its current form, reasons for this could be that the voids in the materials are too wide for effective capillarity; absorption of the solvents into the polymer matrix may further complicate the measured imbibition profile. Another possible reason is the differences between the sizes of the interconnecting pores in scaffolds with varying void sizes; this could affect the capillary effect of the test liquids through the material. The repeatability of the results and the similar patterns observed with the different liquids suggest that if these issues could be quantified and incorporated into the Washburn equation, it may be possible to generate useful results for similar materials.

Introduction

Surface energy is an important property of biomaterials. The surface energy of a material plays a crucial role in a material's interaction with the surrounding biological environment. In the seconds following placement within a biological system, the interactions between the biomaterial and the environment are controlled by surface energy and involve protein adsorption. Since it is via extracellular proteins and cell surface receptors that a tissue will interface with an implant, material–protein interactions therefore play an important role in dictating a material's biocompatibility.

A measure of the surface energy of a material is its hydrophilicity, which can be quantified as the degree of wettability of a material with water. Wettability can be measured by analysing contact angles that liquids of known surface energy make with the material in question. The common techniques for measuring contact angles and thus hydrophilicity such as the Wilhelmy or the sessile drop methods assume that the surface of the material is smooth, flat and uniform [1]. These techniques have been employed with success in characterising the surface energy of biomaterials [2, 3]. However, there are biomaterials to which these techniques are unsuitable as they are not smooth, flat or uniform in their structure. This is the case with porous biomaterials, which are the focal point of many tissue engineering technologies. Often materials can be produced in a form that is suitable for testing with the traditional techniques of wettability measurement, but in many cases the actual production of a porous material can involve changes to the surface chemistry of the material and thus its surface energy. It is this quandary, which is the basis for this work: finding a method of measuring hydrophilicity of porous 3-D biomaterials.

The origin of the technique used in this study was a piece of work published in 1921 by Edward Washburn, which described the dynamics of capillary flow [4]. This publication discusses capillary flow in terms of the contact angle of the liquid on the material forming the capillary. Further to this, it describes an analysis of liquid penetration into a porous body by assuming the body could be described as a number (n) of capillaries with radii r_n. There have been many studies, which have employed the Washburn's technique to analyse the wetting properties of porous materials, but these reviews focus primarily on powder materials, which have very small capillary spaces [5–11].

This work describes the application of the Washburn technique to provide an estimate of the surface energy of porous polyetherurethane scaffold materials.

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The Washburn technique is based on the following equation [12, 13]:

$$W^2 = K\frac{\rho^2\gamma\cos\theta}{2\eta}t \quad (1)$$

where W is the weight of the sample, K is the geometric factor (a material constant), ρ is the density of liquid, γ is the surface tension of liquid, θ is the contact angle of liquid, η is the viscosity of liquid and t is the time

An important element of the Washburn equation is the geometric factor, K. The basis of this constant is from the fact that the Washburn equation is an extension of simple capillary theory; K has the following definition [12, 13]:

$$K = Cr\varepsilon^2\left(\pi R^2\right)^2 \quad (2)$$

Where C is a constant, which allows for the tortuous path of the flow through the capillary network (i.e. not necessarily a straight line), r is the mean radius of the capillary tubes, ε is the porosity of the sample, and R is the mean hydrodynamic radius of the sample. Since these values are not easily measured, they are grouped as a constant for a given material.

An important observation of this model is the fact that liquids displaying a contact angle of more than 90° will not spontaneously wet the material. This is because there should be a net force acting to draw the liquid front onto the material in order to wet it; this is not the case if the contact angle is greater than 90°, hence the cos θ term which will return a value of zero for angles greater than this.

Materials and method

The materials used in this study are a group of porous polyether polyurethane (PEU) biomaterial samples manufactured by MedNova Ltd. They are produced in a range of void sizes (Table I).

The molecular structure of the PEU is assumed to be exactly the same for each set of samples since the same formula was used to produce all of the void size range. Therefore, the only variable to change between materials is the void size, which should produce a difference in, K, between samples.

Equation 1 states that the weight of a porous sample will increase with time, at a rate that depends on the properties of the liquid, the geometry of the sample and also the contact angle between the liquid and the material. To observe these effects, a porous sample is suspended from a sensitive microbalance (CDCA-100F (Camtel Ltd, UK)) and brought into contact with the surface of a test liquid of known properties. The microbalance measures changes in weight of the sample as liquid is drawn into the voids of the material, and records this against time. The porous sample is maintained in the same position, whilst the liquid is brought into contact by a movable stage. This has the effect of minimising any noise in the balance thus making it very sensitive to changes in weight. When the sample contacts the liquid there is a change in weight as the liquid is drawn into the sample; this stops the stage moving and the sample is held in a constant position just touching the surface of the liquid (therefore, there are negligible buoyancy effects).

As the experiment continues the sample increases in weight as more liquid is drawn into the voids in the material. The graph of W^2 plotted against t, should show a straight line with a gradient as shown in Equation 3.

$$\text{Gradient} = \frac{K\rho^2\gamma\cos\theta}{2\eta} \quad (3)$$

All the above terms should be constant and not time dependent. However, experimentally this is not the case and a curve is produced as shown in Fig. 1.

The initial portion of the graph represents the imbibition of liquid into the sample. The very flat portion of the curve represents the filling of some of the smaller voids and pores in the material. Therefore, it is the initial, faster imbibition curve, which is of interest as it is this portion of the curve that corresponds with the wetting of the sample.

In the Washburn equation, there are two unknown quantities, the geometric factor (K) and the contact angle (θ). For Washburn experiments it is necessary to determine the geometric constant of the material before the contact angle against a known liquid can be measured. The geometric constant is unique for each material since it depends on several factors (void size, sample size, porosity). To measure the geometric constant, the other variable, contact angle, needs to be eliminated from the equation. A liquid, which totally wets the sample leading to a contact angle of zero, was used to do this $(\cos\theta = 1)$. n-Hexane is a non-polar solvent with a very low surface tension and is the liquid of choice for the assumption of total wetting. The gradient of the imbibition curve with a totally wetting liquid is used to measure the material constant, since all of the other terms are known constants.

Before testing, the porous PEU samples were considered to be hydrophobic so it was expected that the contact angles of water with these materials would be

TABLE I Mean void size of polyetherurethane foam samples

Mean void size (μm)
326
251
232
219
182
181
163

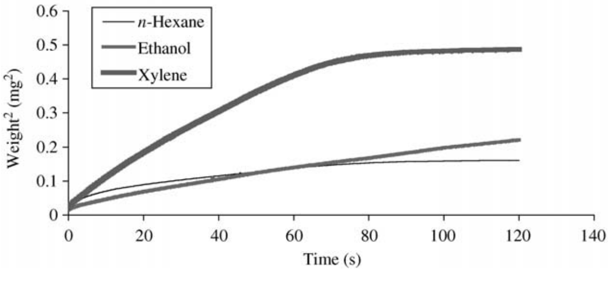

Figure 1 Absorption curves for 326 μm LDPEU with n-hexane, ethanol and xylene.

TABLE II Liquids used for the experiments and their properties

	Surface tension (N/m)	Density (g/m^3)	Viscosity ($N\,s/m^2$)
n-hexane	0.0184	661 000	0.000326
Ethanol	0.0223	785 000	0.001100
Xylene	0.0289	867 000	0.000620

TABLE III Material constant values determined using *n*-hexane

Void size (μm)	Gradient	*K*
326	0.001667	1.35E-16
251	0.0575	4.66E-15
232	0.009033	7.33E-16
219	0.003433	2.78E-16
182	0.0134	1.09E-15
181	0.010567	8.57E-16
163	0.035467	2.88E-15

greater than 90°. Experiments confirmed this, as imbibition curves were not produced when samples were tested with water. However, it was possible to test the materials with other liquids to give information on their surface energy (Table II). A Zismann plot of the contact angles vs. surface energy of the liquids could then be plotted and an estimate of the contact angle with water calculated for comparisons. For all the test liquids, the gradient of the initial portion of the curve is given by the relationship described in Equation 3.

n-Hexane was used to determine the materials' geometric constant whilst the other two liquids (ethanol and xylene) would give a value of contact angle for different surface energies.

Results and discussion

Fig. 1 shows absorption curves typical of those produced by all of the samples being tested with *n*-hexane, ethanol and xylene. They all show a distinct straight-line portion, which corresponds to the rise of the liquid into the material. The plateau on the graph corresponds to when the material has absorbed its maximum amount of liquid.

The gradients of the imbibition sections (straight lines) of the curves were measured. From the Washburn equation, the gradient is described by Equation 3.

The value of K and $\cos\theta$ are of interest since these are the unknown variables. Rearranging the equation for these terms gives Equation 4:

$$K\cos\theta = \frac{2\eta\,\text{gradient}}{\rho^2\gamma} \tag{4}$$

Determining geometric constant, *K*

n-Hexane has an extremely low surface tension and is thus considered to completely wet the material; exhibiting a contact angle of zero. Using *n*-hexane as the testing liquid enabled K to be determined for the materials, since the value of $\cos\theta$ will equal 1 and all other terms were known, this gives Equation 5.

$$K = \frac{2\eta\,\text{gradient}}{\rho^2\gamma} \tag{5}$$

Multiply the gradient of the *n*-hexane absorption curve by the value shown in Equation 6.

$$\frac{2\eta}{\rho^2\gamma} = 8.1\times10^{-14} \quad (\text{for } n\text{-hexane}) \tag{6}$$

This gave the values of K for the materials being investigated, the results are summarised in Table III. These values of K for the different materials were used to calculate the contact angle of the various liquids on the biomaterial samples.

Contact angles with ethanol and xylene

The gradients measured were for the imbibition section of the curves. The value of K is known, so the equation can be rearranged for $\cos\theta$ as in Equation 7.

$$\cos\theta = \frac{2\eta}{K\rho^2\gamma}\text{gradient} \tag{7}$$

Therefore multiplying the gradient by the value in Equation 8, for each of the liquids, gave a value for $\cos\theta$.

$$\frac{2\eta}{K\rho^2\gamma} \tag{8}$$

The results with ethanol, Equation 9, and xylene, Equation 10, for each material are summarised in Fig. 2.

$$\frac{2\eta}{K\rho^2\gamma} = \frac{2\times0.0011}{K_{\text{Material}}785\,000^2\times0.0223} = \frac{0.0022}{K_{\text{Material}}1.37\times10^{10}} \tag{9}$$

$$\frac{2\eta}{K\rho^2\gamma} = \frac{2\times0.00062}{K_{\text{Material}}867\,000^2\times0.0289} = \frac{0.00124}{K_{\text{Material}}2.17\times10^{10}} \tag{10}$$

Observation A

The results showed some anomalies: the values of θ cannot be calculated. This is because the value of $\cos\theta$ is greater than 1. This is shown in Fig. 2; where the value of $K(\equiv K\cos\theta)$ with *n*-hexane is lower than $K\cos\theta$ with the other liquids. A possible explanation is if ethanol and xylene are penetrating the material faster than *n*-hexane. Consider the Washburn Equation 1; rearranged, it can be used to consider the volume of liquid that penetrates the material, Equation 11.

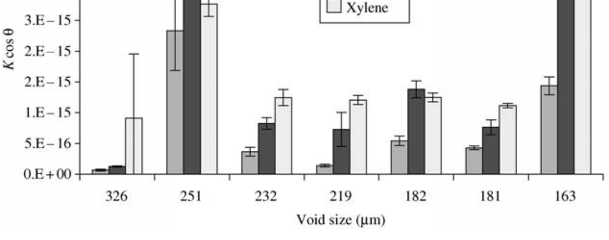

Figure 2 Graph showing $K\cos\theta$ values for each material and test liquid.

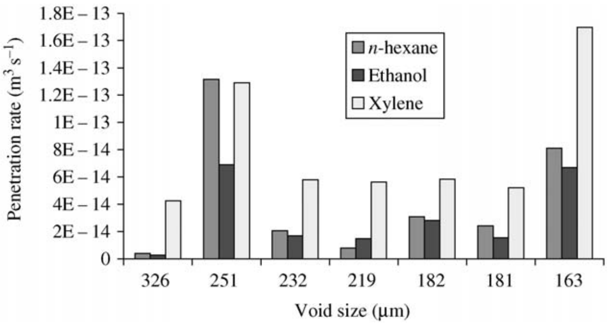

Figure 3 Graph showing the liquid penetration rates for each material and test liquids.

$$V^2 = \frac{K\gamma\cos\theta}{2\eta}t \tag{11}$$

where V = volume of liquid (m^3)

The gradient of the V^2 vs. t graph gave an estimate of the rate of penetration of the material by the liquid. Fig. 3 summarises this data as a graph and demonstrates that the penetration of xylene into the biomaterial sample occurs much quicker than for *n*-hexane in most cases. The only explanation for this is that factors other than contact angle are more important for the penetration of liquids into the biomaterial sample. The Washburn model may not fully explain the phenomena observed in porous materials of this size and type; i.e. between approximately 326 and 163 μm.

Although the pattern is not perfectly clear, the order of penetration rates appears to be xylene, hexane and ethanol. This is not explained by any of the parameters in the equation (i.e. ρ, γ or η) as they do not follow this pattern.

However, even for the samples that are penetrated quicker by *n*-hexane than the other test liquids, a value of θ still cannot be calculated. But in the Washburn equation, the rate of penetration is not the only factor in determining the material constant or contact angle; viscosity (η) and surface tension (γ) are used to calculate $K\cos\theta$ also. That is, liquids with similar densities but different surface tensions would occupy different volumes of a material at a given time. The Washburn equation calculates the material constant using this assumption. If there were another factor, which caused the penetration to occur differently, this would upset the calculations. Perhaps the differences between Figs. 2 and 3 suggest that the Washburn model used is unsuitable in this scenario.

Observation B

There is a further discrepancy with the data; the absorption data did not follow a pattern related to void size. The different geometrical features of the test materials should be normalised by the material constant; K. As explained by Equation 2, this constant incorporates geometric parameters such as capillary size, sample geometry, winding capillary path and porosity.

Since the sample size of each of the materials is the same, only capillary size (r), porosity (ε) and tortuousness (C) will vary. Capillary size is directly proportional to void size, but this does not explain the pattern observed in absorption rates. Therefore, it may be that parameters such as the porosity and tortuousness of capillaries, which are not directly related to void size, are significant factors in absorption rates. However, these factors are related to the interconnectivity of the porous structure, that is, the number of pores that link adjacent voids to create open communication between voids. This explanation is appreciated when images of the different biomaterial sample types are observed, as in Fig. 4. It can be seen between samples of different void sizes, that the voids do not interconnect in a similar manner between different samples.

Observation C

The actual volume of the sample occupied by the liquid should equal the porosity of the sample. Making a graph of V^2 vs. t and taking a reading of the top of the plateau region of the curve can calculate this estimate of porosity. The Washburn equation was used in terms of volume as described by Equation 11. Fig. 5 is an example from the 232 μm void size biomaterial sample.

It is clear from Fig. 5, that the different liquids occupy different volumes of the sample. If the liquids penetrate the sample at all, then they should occupy the same volume of space within the material. However, this is clearly not the case, and we can see for example, that xylene appears to occupy more of the sample than hexane. There are two possible explanations for this.

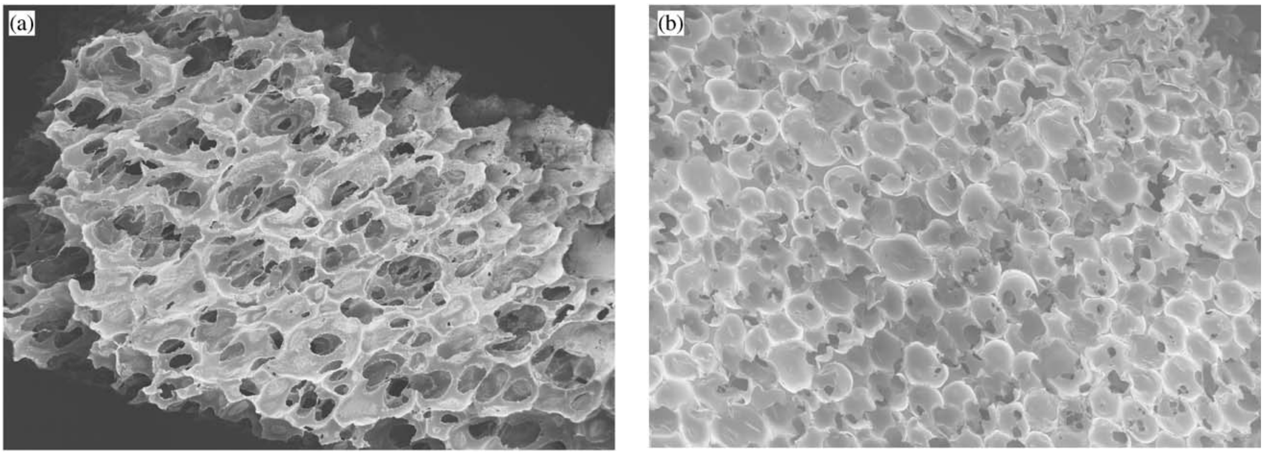

Figure 4 Images of separate foams with different interconnectivity between voids.

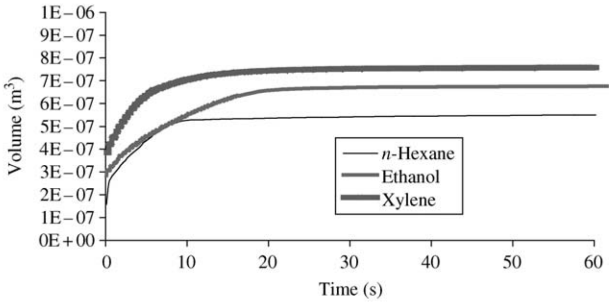

Figure 5 Differences in volume occupied in sample by different test liquids.

First the liquids that occupy a higher volume of the sample do this by causing the material to swell and thus absorb more liquid. The second explanation is that the liquids occupying a greater volume are able to penetrate further into the material such as in blind pores for example.

Conclusion

The use of the Washburn equation as described, was not suitable for application to this biomaterial system.

One of the contributory factors is thought to be the size of the voids and pores in the porous material; they may not allow sufficient capillary forces to be generated to allow the complete imbibition of the test liquids predicted by Washburn's equation.

Another contributory factor may be that the swelling of the polymer causes different absorption behaviour than expected under Washburn's equation. That is, liquid absorbed into the polymer matrix itself, this is not described by Washburn's equation, and would complicate the absorption behaviour.

The data presented does show, however, that the results are reproducible for materials of a given void size. The fact that the data does not relate to void size suggests that factors such as the interconnectivity of the porous structure need to be accurately described and incorporated into Washburn's equation for it to apply to porous structures of this size and type.

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