Factors Affecting the Morphology and Mechanical Properties of a Coagulated Thermoplastic Polyurethane

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ABSTRACT: One of the principal failures of current vascular prostheses is compliant mismatch between the host arteries and prostheses at the anastomoses. Current commercial vascular prostheses are fabricated using either microporous poly(tetrafluoroethylene) or poly(ethylene terephthalate), both of which are incompliant in comparison with the host artery. Thermoplastic polyurethanes that are inherently compliant, therefore, offer the potential for use as vascular prostheses. This article presents a new approach to produce a compliant microporous thermoplastic polyurethane material using a coagulation coating technique. A study on the factors affecting the physical and structural behaviors based on porous polyurethane membranes were investigated. The effects of coagulants and coagulation temperatures on the properties of the coagulums were evaluated and the mechanism for the formation of microcellular structures was discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1947–1954, 1997

Key words: thermoplastic polyurethane; vascular prosthesis; compliant; coagulants

INTRODUCTION

The most successful treatment of obstructive arterial disease of the lower extremities is autogenous venous bypass.[1,2] While this technique is successful, many patients do not have suitable lengths of saphenous veins, and branching or disease may make them unsuitable for long bypasses. Although polymeric materials including the poly(ethylene terephthalate) and poly(tetrafluoroethylene) have been found suitable for large internal diameter prostheses, very low patency is achieved with small vessels less than 5 mm internal diameter and of long length.[3–5]

One of the principal cause for the low patency in small-diameter prostheses is that current prostheses, though microporous, are incompliant. Host arteries are inherently compliant, and it is known that the natural arterial flow of blood to the extremities of the body would be seriously hindered if there are compliance mismatch at the anastomses.[6] It is, therefore, important that the ideal small diameter vascular prostheses should have compliance matching with the host artery and must be constructed from a polymeric material that is physiologically inert. The polymer of choice must be capable of suturing, the stitches must not tear and the suture holes must be sealable. A further requirement, particularly at body joints, is that the prosthesis must not collapse on bending, thereby restricting blood flow. Additionally, for a medical implant, the polymer must be capable of being sterilized without destroying its material properties. While many polymers have been used as body implants, the polyurethane materials appear to satisfy many of the specific requirements and also to offer the greater advantages for fabrication of arterial prostheses. They are capable of being manufactured in a large variety of chemical types with a very wide range of properties and the materials may be fabricated by procedures that offer diversity of artifacts. Many advocates of synthetic materials for arterial pros-

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thesis advise the use of porous structures that after implantation can be lined with endothelial tissues. Many prostheses have been designed for this purpose and consist of microcellular porous structures.[7–9]

The approach adopted here is to design a method of fabricating a polyurethane material that is both porous and having a smooth flow surface. There are many methods of producing cellular or porous structures of a range of densities in polyurethanes. Gas blowing by the reaction of an isocyanate with water form the basis of most foam formation systems.[10] This *in situ* foaming process involves concurrent polymer formation, gelation, and gas formation, which needs to be carefully balanced to generate an acceptable foam structure. For consideration as arterial prostheses, these foams are usually too low in density, highly porous, have large cellular structures, and are generally low in mechanical performance. An alternative approach of obtaining microcellular (or porous) materials is coagulation coating, which is being investigated here.

Coagulation Process

The most common method of producing microporous materials is by coagulating a polymer solution in the presence of a nonsolvent liquid (i.e., coagulant), water, or vapor, usually miscible with the polymer solvent, producing a microporous permeable structure. One of the earliest examples of these methods was biological filters made by coagulation of cellulose acetate or cellulose nitrate from acetone–acetic acid solutions using water.[11] A number of other polymers, for example, poly(vinyl chloride) and poly(acrylonitrile), have been used in this way to make leatherlike coating and shoe insole materials.

Another fabrication technique, a variant of the above, involves the incorporation of a water-soluble inorganic salt or organic sugars (fillers) into the polymer solution, coagulating the polymer in a suitable coagulant and subsequently leaching out the fillers with water. In this study the effects of coagulation temperature and coagulants on the microcellular structures and mechanical properties of the polyurethane are being investigated.

EXPERIMENTAL

Materials and Chemicals

Polymer

A proprietary thermoplastic polyether–polyurethane with a molecular weight in the order of 21,000 g/mol (determined by gel permeation chromatography, GPC) was used in this study. This polyurethane is soluble in *N,N*-dimethyl acetamide (DMAc) and tetrahydrofuran (THF) solvents. All the chemicals used are general purpose laboratory grades supplied by BDH, UK.

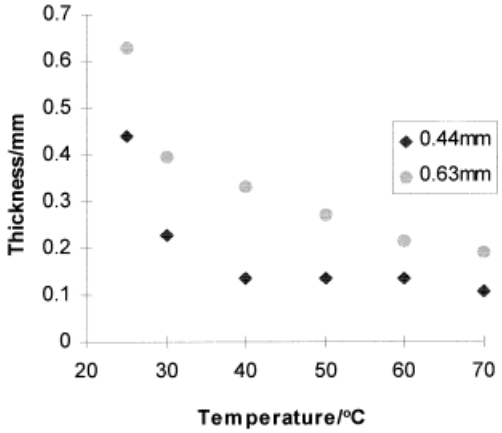

Figure 1 Effect of water coagulation temperature on final coagulum thickness.

Polymer Solution

A 20% solution of polyurethane was prepared by placing 80 g of the polymer into a 1-L round-bottomed flask containing 320 g of DMAc. The mixture was continually stirred at ambient temperature until a gel-free, homogeneous solution was formed. The solution was degassed prior to storage for later use.

Preparation of Microcellular Membranes

Approximately 50 mL of 20% polyurethane solution was degassed in a vacuum oven (30 mmHg) at room temperature until no further bubbles were liberated from the solution. The solution was then carefully poured onto a clean, dry glass plate ($27 \times 20 \times 0.5$ cm). A doctor blade of known clearance height was used to spread the solution evenly over the plate. Two different wet thickness coatings of 0.4 and 0.63 mm were investigated. Different types of porous sheets were produced by changing the conditions of coagulation. Variation carried out were (1) coagulating in distilled water at temperatures between 30 to 70°C, (2) coagulating in different coagulants (methanol, ethanol, propan-2-ol), and (3) coagulating in various concentrations of aqueous propan-2-ol coagulants [between 10 to 90% (volume) water].

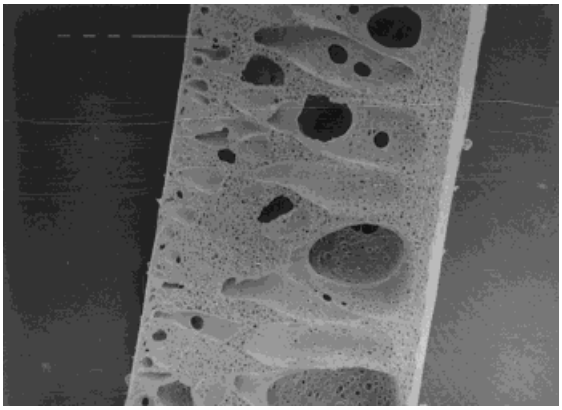

Figure 2 Scanning electron micrograph of coagulum formed in water at 30°C (magnification × 150).

Coagulation Procedure

To coagulate the polyurethane solution, the coated plate was carefully immersed in the coagulant and allowed to coagulate overnight. The coagulum was then carefully removed from the glass plate and transferred to a bath containing distilled water to allow excess solvent to leach out of the coagulum. All the coagulums were kept in distilled water until required for further experiments.

EVALUATION

Thickness Measurements

The average thickness of each porous sheet (coagulum) formed under different coagulation conditions was determined using a bench micrometer (Mercer, UK, model 102). Quintuplicate measurements were made for each sample strip and a total of 20 strips were taken from coagulated sheets produced using the same conditions.

Mechanical Testing

Tensile testing were carried out using the Universal Tensile Testing equipment, model 1121. Coagulated sheets were cut into dumbbell-shaped specimens, according to BS 2782 method 320A. All the samples were tested wet at 25°C. The rate of strain was set at 200 mm/min, and samples were tested until breaking point. The secant Young's modulus at 20% strain values were determined.

Scanning Electron Microscopy (SEM)

Samples were gold-sputtered and examined using a JOEL scanning electron microscope.

Reactions Between DMAc and Coagulants

The primary purpose of this experiment was to measure the heat of reaction between the solvent and the coagulants. The heat of reaction was measured in terms of the temperature change in the solution mixture. It was believed that the change in the temperature of the reaction mixture might be responsible for the formation of large tear-shaped structures in the coagulums.

Distilled water (50 mL) was poured into an insulated polyethylene beaker. The temperature of the water was recorded using a mercury thermometer (accuracy ±1°C). An equal amount of DMAc, at a known temperature, was then added to the beaker containing the water and rapidly stirred. The maximum temperature of reaction was recorded using the thermometer. The same procedure was repeated for methanol, ethanol, and propan-2-ol.

RESULTS

Effects of Coagulation Temperature

Figure 1 shows the final thickness of the coagulum as a function of the water temperature. The plot shows a decrease in the final thickness of the coagulums with increasing temperatures of water. When the solution has a thin initial cast thickness (<0.44 mm), the final thickness of the coagulum reaches an asymptotic value (~0.1 mm)

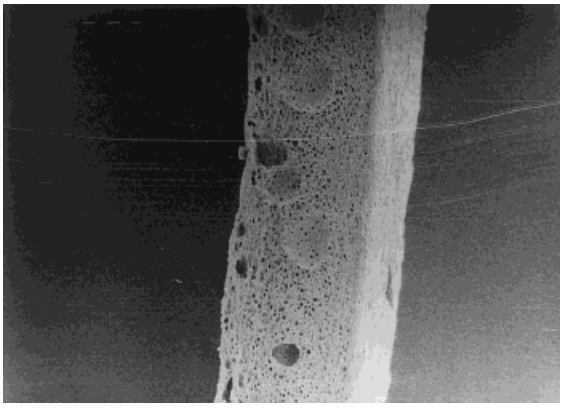

Figure 3 Scanning electron micrograph of coagulum formed in water at 70°C (magnification × 150).

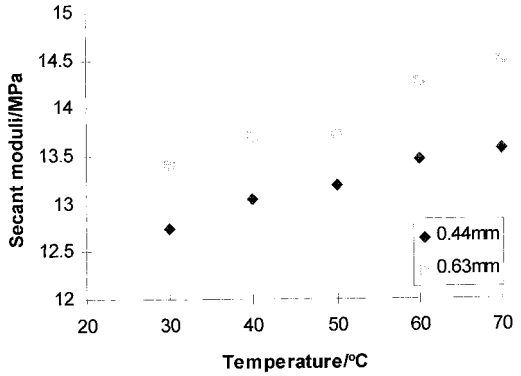

Figure 4 Effect of water coagulation temperature on secant moduli of final coagulums.

at coagulation temperature at approximately 40°C. However, for solutions with thicker cast thickness, higher temperatures of coagulation are required to achieve the asymptotic values. (This could be associated with the problem of diffusion of coagulant into the solution at lower temperatures.)

Figures 2 and 3 show the SEM micrographs of the cross section of two samples coagulated in water at 30 and 70°C, respectively. It is observed that the effect of coagulation temperature has significant impact on the cellular structure present in the substructure of the coagulum. Generally, increasing the temperature of coagulation reduces the occurrence of the tear-shaped structures that are present are reduced in size. A comparison of SEM micrographs Figures 2 and 3 shows the disappearance of the tear-shaped structures for sample coagulated at 70°C.

The effect of the coagulation temperatures on the coagulums is also reflected in the secant Young's modulus as shown in Figure 4. It is found that the secant Young's moduli of the coagulum increase with the coagulation temperatures of water. This is expected as the porosities of the coagulums decreased with coagulation temperatures, the moduli of elasticity would also increase as the densities of the coagulums approached that of the solid film.

Effects of Coagulants

Unlike coagulation in water, it is noted that the rate of coagulation in alcohols are very much reduced. The rate decreases from methanol, ethanol, and propan-2-ol at ambient temperature, respectively. The effects of using various alcohols as coagulants on the final thickness of the coagulums

Table I Effect of Coagulant on Coagulum Thickness

Coagulant	Wet Thickness (mm)	Final Thickness (mm)
Methanol	0.44	0.13
Ethanol	0.44	0.10
Propan-2-ol	0.44	0.08

are summarized in Table I. Although there is no significant difference between the final thickness of the coagulum formed in methanol, ethanol, and propan-2-ol, the general trend shows that the final thickness of the coagulum decreases with the higher alcohols.

The most dramatic effect of coagulating the polyurethane solution in different alcohol is observed in the substructure of the coagulum. Figures 5, 6, and 7 show the SEM micrographs of the substructures of coagulums formed in methanol, ethanol and propan-2-ol, respectively. Comparing the substructures with those found in coagulum formed from water, coagulums formed in alcohols have no tear-shaped structures, and there is significant reduction in the numbers of microporous structures. In the case of propan-2-ol, the coagulum is almost a solid film.

Effect of Aqueous Propan-2-ol

Figure 8 shows the effect of solutions of various concentrations of aqueous propan-2-ol has on the final thickness of the coagulum. The final thickness of the coagulums decreases with increasing concentration of propan-2-ol in the coagulant.

Figures 9 and 10 show the SEM micrographs

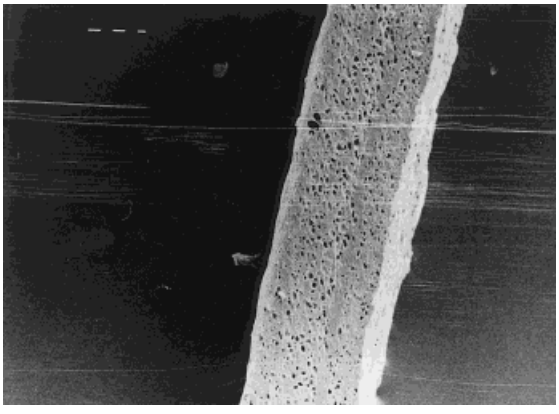

Figure 5 Scanning electron micrograph of coagulum formed in methanol (magnification × 150).

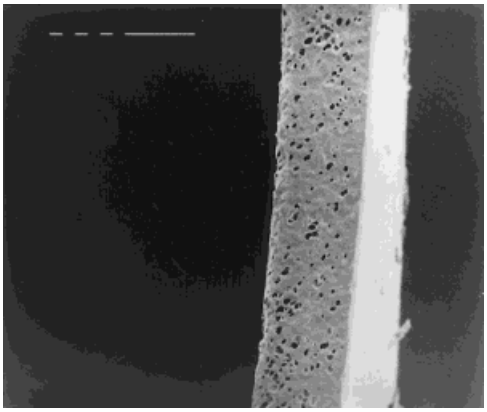

Figure 6 Scanning electron micrograph of coagulum formed in ethanol (magnification × 150).

of coagulums formed in 60 and 10% (volume) aqueous propan-2-ol, respectively. The following changes in the cellular structures due to the various concentrations of propan-2-ol are observed: (a) the reappearance of the microporous structures, (b) the reappearance of the tear-shaped structures when the coagulant contains about 50% of distilled water, and (c) the number of tear-shaped structure increases with the concentration of distilled water present in the coagulant system.

Temperature of Reaction Between Solvent and Coagulants

The results of temperature change due to the reactions between the alcohols and the solvent is shown in Table II. It can be seen that the temperature of reaction decreases from water to propan-2-ol, and this can be correlated to the final thickness of the coagulum as well as to the size and the cellular structures. As the temperature of reaction increases, the thickness of the coagulums also increases with the appearance of large tear-shaped structures. The mechanism of the pores and tear-shaped structure formation will be discussed later.

DISCUSSIONS

Mechanism of Microcellular Formation

Solvent Dilution Model

Unlike the thermal expansion processes, the mechanism involved in the formation of microporous structures by coagulation method is ill-defined. The mechanisms for coagulation of polymer solution in a suitable coagulant, usually water, or by any other phase-inversion techniques, have been conflicting.[12,13] However, the solvent dilution hypothesis[14] offers a feasible mechanism for the formation of microporous structures by coagulation. This hypothesis is relevant to the present work because it is based on polyurethane solution and it emphasizes on the role of coagulants.

The solvent dilution hypothesis states that when a solution of polyurethane is immersed in a coagulant the solvent in the solution is diluted by the coagulant. This solvent dilution will continue until the residual solvent in the solution cannot maintain all the components of the system in a homogenous solution (i.e., the polyurethane coagulates forming a white opaque porous material with a skinned surface). The skin is formed on the surface of the coagulum because of the high polymer density and low level of dilution between the surface of the cast and its interior. Once formed, especially at the upper surface, the skin serves as an osmotic barrier between the polymer solution and the coagulant. This controls the rate of further solvent dilution of the remaining solution in the cast.

The solvent exchange reactions occur simultaneously with the coagulation process because of the solution–coagulant concentration gradient. The departure of the solvent molecules leave voids, giving a porous characteristics to the final product, and localized solvent concentration on the surface of the cast redissolves some area of the skin to leave pores on the surface of the coagulum.

Extended Solvent–Dilution Model

Although the solvent dilution hypothesis is adequate for explaining the occurrence of micropo-

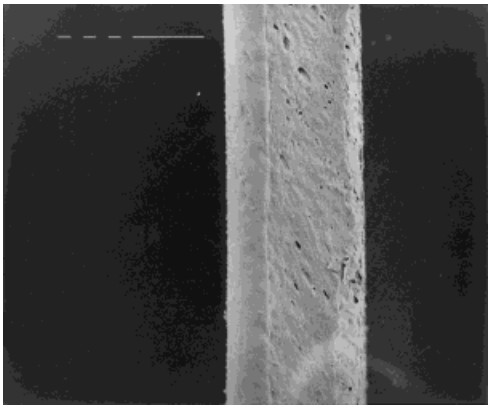

Figure 7 Scanning electron micrograph of coagulum formed in propan-2-ol (magnification × 150).

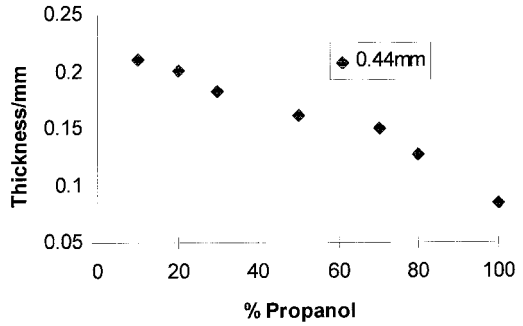

Figure 8 Effect of propan-2-ol concentration on coagulum thickness.

rous structures in the coagulated material, it does not account for (1) the presence or absence of the tear-shaped pores, and (2) the different rates of coagulation in various coagulants. In order to account for these phenomena, an extended solvent–dilution model of microcellular formation is proposed here.

It is believed that the coagulation behavior of the binary polyurethane solution is determined by three probable factors, namely (1) the difference in the solubility parameters (S) between the polymer and the coagulant, (2) the temperature of reaction between the coagulant and the polymer solvent, and (3) the coagulation temperature.

It is generally accepted that the best solvent for a given polymer is one whose solubility parameter is equal or close to the solubility parameter S of that polymer, i.e., $S_1 = S_2$ or $(S_1 - S_2) < 1.7$ to 2.0, where S_1 and S_2 are the solubility parameters of the solvent and polymer respectively.[15] Because the polyurethane dissolves in DMAc solvent, it is reasonable to assume that the polymer has a solubility parameter value close to DMAc, i.e., 11.1 $(\text{cal/cm}^3)^{1/2}$. Table III gives the solubility parameters of the various solvents (coagulants) and their differences compared with DMAc.[15]

When the polyurethane solution is immersed in copious amount of coagulant, the rate of coagulation and the formation of the skin layer depend on the solubility parameter difference between the polymer and the coagulant. It has been observed that the rate of coagulation increases with the difference in the solubility parameter values, i.e., the rate of coagulation decreases from water, methanol, ethanol, and propan-2-ol, in that order. Where there is a minimal solubility parameter difference, as between propan-2-ol and DMAc, a solid, opaque film is formed.

With regard to the tear-shaped features in the coagulum, it has been observed that the coagulant penetration gives rise to fingerlike ingrowths into the coagulating polyurethane solution.[14] This fingerlike ingrowths continue penetrating the solution until a hydrodynamically stable is attained (i.e., the resultant penetrating forces of surface tension and viscosity gradient were no longer capable of halting the "fingers" advancing into the solution). The coagulant, which has diffused through the micropores on the skin layer, then reacts with the solvent in the polymer solution. The formation of tear-shaped structures is dependent on whether the reaction between the solvent and the coagulant is exothermic or endothermic.

When the reaction is exothermic, as in water and DMAc, the rapid rise in the temperature of the coagulating polymer solution causes sudden expansion of air in the fingerlike ingrowths, causing it to expand into tear-shaped structures. The greater the temperature rise, the larger the tear-shaped structures. Where there is little or no change in the temperatures of the coagulating solution, no rapid expansion of dissolved air in the fingerlike ingrowths can occur; hence, no tear-shaped structures. This, therefore, accounts for the disappearance of the tear-shaped structures in coagulums formed in alcohols. This hypothesis is further substantiated by the reappearance of the tear-shaped structures when water is added to the propan-2-ol and there is a good correlation between the number and size of these structures with the amount of water present in the propan-2-ol.

The main effect of increasing the coagulation

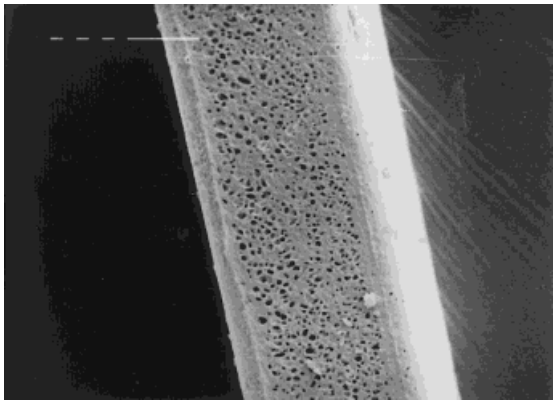

Figure 9 Scanning electron micrograph of coagulum formed in 60% aqueous propan-2-ol (magnification × 150).

Table II Temperature of Reaction Between DMAc and Various Coagulants

Coagulant	Coagulant Temperature (°C)	DMAc Temperature (°C)	Solution Temperature (°C)	Temperature Difference (°C)
Water	19.0	19.0	40.0	+21.0
Methanol	20.0	21.0	25.5	+5.0
Ethanol	20.0	21.0	21.0	+0.5
Propan-2-ol	21.5	20.5	18.0	−3.0

temperature is the reduction of the surface tension of the coagulant. The effect of reducing the surface tension of water increases both the diffusion rate of the coagulant through the porous skin and the coagulation rate. The combination of both effects might be responsible for restricting and even preventing at the early stage the development of the tear-shaped structures. This is also reflected by the high-dimensional shrinkage with coagulation temperature. Therefore, increasing the rate of coagulation reduces the chances of the tear-shaped structures developing. This could account for the reduction in the size and number of these tear-shaped structures with increasing coagulation temperature.

Another probable contributory factor for the decrease in the number and size of the tear-shaped structures with increasing temperatures of the coagulation, in addition to the surface tension of the coagulant explained earlier, is the fact that the amount of dissolved air in the coagulant system decreases with increasing temperatures. Therefore, because there is smaller volume of dissolved air present, at higher coagulation temperatures the extent of air expansion occurring during the coagulation is necessarily reduced.

Hence, through a combination of coagulation temperature and choice of coagulant, the microcellular structures and the mechanical properties of the final poromeric polyurethane can be engineered.

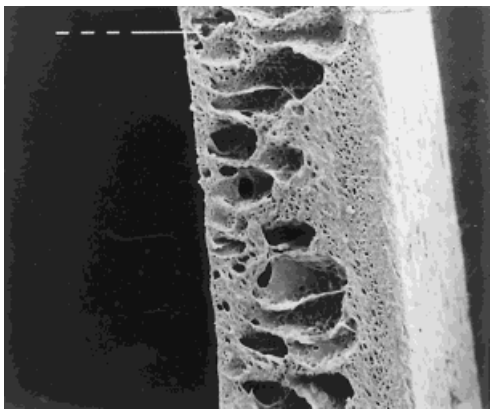

Figure 10 Scanning electron micrograph of coagulum formed in 10% aqueous propan-2-ol (magnification × 150).

CONCLUSION

The effect of coagulant and the coagulation temperatures is found to have pronounced influence over the microcellular structures and mechanical properties of the coagulum. Generally increasing the coagulation temperatures have the same effect as coagulating the polyurethane in simple alcohols, i.e., the occurrence of tear-shaped structures diminishes with coagulation temperature. It is also found that the occurrence of the tear-shaped structures is dependent on the exothermicity of the interaction between the polymer solvent and the coagulant used. The higher the reaction temperature between the solvent and the coagulant, the larger the size of the tear-shaped structures.

In conclusion, the proposed extended solvent–dilution model provided a useful model for under-

Table III Solubility Parameters of Various Coagulants

Coagulant	Solubility Parameter [(cal/cm^3)$^{1/2}$]	Difference (c.f. *N*,*N*-dimethyl acetamide)
Water	23.4	+12.3
Methanol	14.5	+3.4
Ethanol	12.7	+1.6
Propan-2-ol	11.5	+0.4

The solubility parameter of *N*,*N*-dimethyl acetamide is 11.1 (cal/cm^3)$^{1/2}$.

standing the mechanism of microcellular structure formation in polyurethane. There is potential for this technique to be further developed for other medical devices such as artificial skin or membranes, where compliance and control over the porosity are paramount.

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