A Two-Step Method for the Synthesis of a Hydrophilic PDMS Interpenetrating Polymer Network

Anna Hillerström,[1,2] Bengt Kronberg[1,2]

[1]*YKI, Institute for Surface Chemistry, Box 5607, SE-114 86 Stockholm, Sweden*
[2]*Department of Physical Chemistry, Karlstad University, SE-651 88 Karlstad, Sweden*

Received 10 October 2007; accepted 18 March 2008
DOI 10.1002/app.28485
Published online 8 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A hydrophilic PDMS (polydimethylsiloxane) surface was formed by the synthesis of an interpenetrating polymer network (IPN) in a two-step process. In the first step, PDMS was loaded with crosslinker and initiator using a solvent that swells the PDMS. In the second step, the PDMS sample was submerged into a solution containing the hydrophilic monomer followed by a UV-polymerization step. The choice of solvent in the second step is critical to obtain a hydrophilic surface. It can be concluded that the solubility parameter of the solvent should be above a threshold value. Hence, in the second step only sufficiently polar solvents will result in hydrophilic PDMS-IPNs. These principles are illustrated by using *N*-vinyl-2-pyrrolidone as the hydrophilic monomer forming PVP/PDMS-IPNs. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3059–3067, 2008

Key words: interpenetrating polymer networks (IPN); silicones; hydrogels; thermodynamics; synthesis

INTRODUCTION

Crosslinked polydimethylsiloxane (PDMS) is a very versatile material and can be used in a variety of applications because of its chemical and physical properties, that is, optical, viscoelastic, and rheologic. The material is also inert, nontoxic, and it is therefore considered to be biocompatible such that it is widely used in the medical device industry. Crosslinked PDMS is also a flexible material because of Si—O—Si bonds in the repeating unit of the molecule. Furthermore, it exhibits good thermal and chemical stability as well as high oxygen permeability and transparency.[1] In addition, PDMS has a much lower surface energy value than that of other synthetic polymers (16–22 mJ/m^2, which is approximately 10 units lower than that of other synthetic polymers).[2] However, as PDMS is relatively hydrophobic, it would be advantageous to increase the wettability of such surfaces to enhance the functionality as a biomaterial, for example, catheter and contact lens applications.[3]

Improving the wettability of PDMS is challenging because of its extremely low surface energy. Some common surface modification techniques to obtain a hydrophilic substrate include surface grafting, corona, radio frequency (RF) plasma, and laser treatments.[4–6] However, typically these methods do not prevent reorganization of head groups at the surface and extra steps, specialized equipment and complicated procedures can increase overall manufacturing costs. An alternative method is via bulk modification where suitable polymer blends and copolymers can be included, during fabrication but such techniques have also shown drawbacks, that is, phase separation.[7]

Another option for modifying PDMS is to form an interpenetrating polymer network (IPN). An IPN is a combination of two or more polymers, at least one of which is crosslinked, and where the physical entanglements of the polymer chains improve both the bulk and surface stability of the material.[8] One of the advantages of using an IPN is the possibility of combining different polymer properties, while at the same time minimizing any incompatibility effects. Therefore, this approach avoids the need to synthesize new materials or to develop additional processing steps.

To overcome the low surface energy of PDMS it must be combined with a more hydrophilic polymer. For an IPN, the adhesive forces between the polymer chains are improved resulting in a more stable structure than a film of hydrophilic polymer on crosslinked PDMS. This article investigates combining polyvinylpyrrolidone (PVP) and PDMS in an IPN to retain the mechanical properties of PDMS while improving the overall wettability by using PVP. The synthesis of PDMS-IPNs using a number of other hydrophilic polymers has already been reported in

Correspondence to: Anna Hillerström (anna.hillerstrom@surfchem.kth.se).

Contract grant sponsors: The Swedish Knowledge Foundation and Linde Gas/AGA AB.

the literature.[9–11] It has been shown that in the case of poly(2-hydroxyethyl methacrylate (PHEMA) the contact angle decreases from 105.6° to 61.5° when a 60/40 wt % (PHEMA)/PDMS-IPN was synthesized.[9] In another study, an advancing contact angle of 60° was reported using poly(*N*-isopropylacrylamide) (pNIPAAM) to investigate a PNIPAAM/PDMS-IPN combination.[10] In the present study, the water soluble polymer PVP has been chosen for its relative biocompatibility and due to the fact that it is widely used in pharmacy, cosmetics, and medicine.[12] Biomedical applications of crosslinked PVP already in use today include contact lenses. In contact with aqueous solution PVP forms a hydrogel with the ability to absorb large quantities of water, up to 60% of its weight, depending on the degree of crosslinking.[13,14] Conversely, one of the main drawbacks of hydrogels is poor mechanical stability in the swollen state.[15]

The aim of this work is to obtain a hydrophilic surface of crosslinked PDMS by forming a homogenous film of PVP on the surface as well as crosslinking PVP inside the PDMS to form an IPN. Because of large differences in chemistry between the two polymers, this has to be achieved via a two-step process. The first step involves impregnating the PDMS with photoinitiator and crosslinker using a suitable solvent. The second step is to submerge this preswollen and impregnated PDMS in a solution of NVP (*N*-vinyl-2-pyrrolidone) and solvent followed by polymerization. The reason for using a two step procedure is based on a thermodynamical approach, whereby the selection of solvent required to swell PDMS and the solvent used for polymerization of the monomer, NVP, is very crucial. A suitable solvent for PDMS will not necessarily be the same for PVP, which argues in favor of performing the process in two steps to obtain a hydrophilic PVP-surface on the PVP/PDMS-IPN. It should be possible to apply the same process to a range of other incompatible polymer pairs, for example, IPNs of PDMS and other hydrophilic polymers.

EXPERIMENTAL

Materials

PDMS elastomer (0.51 mm thick sheets having 50 shore A hardness) was kindly supplied by Mentor Corporation, the Netherlands. *N*-vinyl-2-pyrrolidone 99%, stabilized with 0.01% NaOH, was obtained from Aldrich, Germany, for use as the hydrophilic monomer. A mixture of mono- and bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide called Irgacure 2100 (Ciba Speciality Chemicals, Switzerland) was used as the photoinitiator. The crosslinker was triethyleneglycol dimethacrylate, (TEGDMA) 95%, stabilized with approximately 80 ppm hydroquinone (Aldrich, Germany). The solvents used in this study were toluene (p.a., Merck, Germany); ethanol (99.7%, Solveco Chemicals AB, Sweden); *n*-hexane (p.a., Merck, Germany); diethyl carbonate (99%, Aldrich, Germany); cyclohexane (p.a., Merck, Germany); and distilled water. All materials were used without further purification.

Methods

Synthesis procedure of PVP/PDMS-IPN

PDMS discs (1 cm diameter) were immersed in a homogenous solution of Irgacure 2100 (14 wt %), TEGDMA (14 wt %) and solvent (72 wt %). The solvents used in the first preparation step were all selected for their ability to efficiently swell PDMS and are listed in Table I. In this way, the photoinitiator and crosslinker were impregnated into the PDMS. It was shown that equilibrium swelling of PDMS occurs after 15 min as no further weight increase was observed. However, during this study, discs were left in solution for 1 h to fully allow a homogenous distribution of the different compounds within the sample.

In the next step, discs were placed in a second solution that typically contained NVP and solvent(s) (50 wt %). Other ratios of NVP in the range of 5–62 wt % and solvent were also investigated. In some experiments, a mixture of ethanol and another solvent was used to increase the solubility parameter of the solution. The degree of swelling in a mixture of ethanol and another solvent (*n*-hexane, cyclohexane, diethyl carbonate, or toluene) was evaluated by measuring the linear extension of the PDMS samples in the solutions after 1 h. It was concluded that 30 wt % of the swelling solvent in the solution was required to measure any extension of the PDMS sample after immersion in the solution.

Free-radical polymerization reaction was then initiated using a 200 W mercury-xenon lamp, (LC-8, L8868-02, Hamamatsu, Japan) using a constant UV-intensity (I = 300 mW/cm^2) and measured using a light power meter (C6080-03, Hamamatsu, Japan) at 365 nm. During the polymerization, PDMS samples remained in solution using a quartz glass lid to prevent solvent evaporation. The UV-curing was carried out for at least 60 min, to ensure polymerization occurred. All experiments were carried out at room temperature.

The PVP/PDMS-IPN was soaked in distilled water for 24 h to remove any PVP that was not fully crosslinked. The water was replaced a number of times during the extraction until no further reduction in weight for the PVP/PDMS-IPN was observed. Samples were stored in water to maintain the hydrophilic nature of the surface until required for analysis and testing. As a reference control, some samples were prepared in one step, that is, the preswelling of PDMS with Irgacure 2100 and TEGDMA was

TABLE I
The Solvent Combinations Used for Preparation of PVP/PDMS-IPN[a]

Trial no	Solvent (Step 1)	Solvent(s) (Step 2)	$\delta_{solvent(s)}$ $(MPa)^{1/2}$	S (solvent(s))	δ_{tot} $(MPa)^{1/2}$[b]	S (tot)	Appearance of PVP/PDMS-IPN
1	*n*-Hexane	*n*-Hexane	14.9	−141	18.2	−86	Hydrophilic
2	Cyclohexane	Cyclohexane	16.8	−109	19.2	−70	Hydrophilic
3	Diethyl carbonate	Diethyl carbonate	18.0	−89	19.8	−60	-
4	Toluene	Toluene	18.2	−86	19.9	−58	Hydrophilic
5	*n*-Hexane	30 wt % *n*-Hexane + 70 wt % ethanol	23.0[c]	−5	22.3	−18	Hydrophilic
6	Cyclohexane	30 wt % cyclohexane + 70 wt % ethanol	23.6[c]	5	22.5	−13	Hydrophilic
7	Diethyl carbonate	30 wt % diethyl carbonate + 70 wt % ethanol	24.0[c]	10	22.7	−10	Hydrophilic
8	Toluene	30 wt % toluene + 70 wt % ethanol	24.0[c]	12	22.8	−9	Hydrophilic
9	Toluene	Ethanol	26.5	54	24.0	12	Hydrophilic
10	Toluene	Water	47.9	412	34.7	191	Hydrophilic

[a] Solvents in Step 1 correspond to swelling of PDMS to impregnate the oil soluble compounds. Solvents in Step 2 correspond to the solution of monomer and solvent used during polymerization of the PVP/PDMS-IPN. Spreading coefficient, S, is calculated from the solubility parameter for different solutions in Step 2. S (solvent(s)) is calculated for the solvent used in Step 2, whereas S (tot) includes the NVP concentration in the solution (50/50 monomer/solvent). The appearance of the PVP/PDMS-IPNs was evaluated visually.
[b] The total solubility parameter includes the monomer concentration as well as solvent concentration.
[c] $\delta_{mix} = \delta_i x_i + \delta_j x_j$, where x is the weight fraction of component i and j.[16]

excluded. Consequently, all chemicals were mixed in one step and were impregnated during 1 h followed by UV-polymerization. The PDMS sample was kept in the solution during the polymerization reaction. The final PVP/PDMS-IPN was washed, stored in water, and analyzed in the same way as the samples prepared via the two step preparation method.

Determination of PVP percentage and water content percentage in PVP/PDMS-IPN

The amount of PVP in the PVP/PDMS-IPN was calculated from dry weights after extraction in water for removal of residues, as follows:

$$\%\,\mathrm{PVP} = \frac{w_d - w_0}{w_0} \tag{1}$$

where w_d is the weight of the dry PVP/PDMS-IPN extracted in water and w_0 is the initial weight of the PDMS film.

Dry PVP/PDMS-IPNs of known weight were immersed in an excess amount of distilled water at room temperature. After swelling, the PVP/PDMS-IPN in water for more than 24 h and blotting the IPN between two sheets of dust-free tissue paper the uptake in the PVP/PDMS-IPN was calculated from:

$$\%\mathrm{water\,uptake} = \frac{w_s - w_d}{w_d} \times 100 \tag{2}$$

where w_s is the weight of the PVP/PDMS-IPN after swelling in water.

Contact angle measurements

The wettability of the PVP/PDMS-IPN surfaces was mainly characterized by visual inspection due to the fact that they were stored in water throughout the study. Swollen samples were removed from solution and the behavior of the water film on the surface was studied. In certain cases, wettability measurements were carried out using a Dynamic Contact Angle and Absorption Tester, DAT (Fibro 1100, Fibro Systems, Sweden), where contact angles and images, respectively, were obtained. A hydrophilic substrate is indicated when total spreading of a water droplet placed on a sample surface occurs.

ESEM-EDAX

An environmental scanning electron microscope (ESEM) fitted with an energy dispersive X-ray spectrometer (EDAX) (XL30 ESEM TMP, FEI/Philips, the Netherlands) was used to analyze swollen cross sections of PVP/PDMS-IPN. The microscope was operated at 5.9 Torr (90%RH, 5°C) to avoid complete dehydration of the PVP/PDMS-IPN during measurement and elemental mapping of the sample was carried out using 20 kV electron acceleration voltage. Images were recorded at 500× magnification, which was shown to give the best resolution and the EDAX-mapping was performed for a maximum of 45 min. In the case of longer EDAX mapping times samples were found to be fully dehydrated on removal from the ESEM chamber.

RESULTS AND DISCUSSION

Selection of solvents

For the preparation of a hydrophilic PVP/PDMS-IPN, two conditions have to be fulfilled: (1) the crosslinked PDMS must be swollen to impregnate monomer, photoinitiator and crosslinker into the network and (2) an excess of PVP must cover the PDMS surface following polymerization to obtain a water wettable surface. It has been shown that hydrophilic monomer alone is not able to sufficiently swell the PDMS. Hence, a suitable solvent with the appropriate swelling ability and solubility characteristics for NVP/PVP has to be selected. Since PDMS is very nonpolar, the solvent should preferably also be nonpolar. The solubility parameter, δ, is used as a practical guide to identify suitable swelling solvents for polymers. Swelling of a polymer network is best achieved with solvents that have a solubility parameter equal or close to that of the polymer. Since δ_{PDMS} is 14.9 $MPa^{1/2}$ solvents such as *n*-hexane (δ = 14.9 $MPa^{1/2}$), cyclohexane (δ = 16.8 $MPa^{1/2}$), and toluene (δ = 18.2 $MPa^{1/2}$) are good candidates.[17,18] Therefore, these were chosen for investigation in this work.

Obtaining a surface that is wetted by water is more of a challenge. The solubility parameter of PVP is 23.3 $MPa^{1/2}$ (NVP, δ = 21.5 $MPa^{1/2}$), which is significantly higher than the solubility parameter of PDMS.[19] To satisfy the water wettability condition, the surface should have an excess of PVP otherwise the surface will remain hydrophobic. This is not easily obtained because of the very low surface energy of PDMS. A PVP film can only spread on PDMS if there is an energy gain, that is, the total surface energy is lower. The condition for spreading of a film (PVP) on a polymer surface (PDMS) in a solvent is expressed through that the spreading coefficient, *S*, and the value should be positive, that is, $S \geq 0$[20]:

$$S = \gamma_{PDMS/solvent} - (\gamma_{PDMS/PVP} + \gamma_{PVP/solvent}) \geq 0 \quad (3)$$

where γ_{ij} is the interfacial tension between the i and j phases.

If the condition in eq. (3) is not fulfilled, PVP will form droplets on the PDMS surface ($S < 0$). This is illustrated in Figure 1 for the types of PVP/PDMS-IPN that can result following polymerization. Depending on the choice of solvent, the outer layer of the material can either be PDMS or PVP. If $S < 0$, the surface will be covered with PDMS (path 1 in Fig. 1) but if $S \geq 0$ the surface will be covered by PVP (path 2 in Fig. 1).

To predict which solvents to use, it is necessary to convert the interfacial tension of the components to solubility parameters. It can be shown that the interfacial tension between two components is proportional to the χ-parameter (the interaction parameter) of the two components according to the equation[20]:

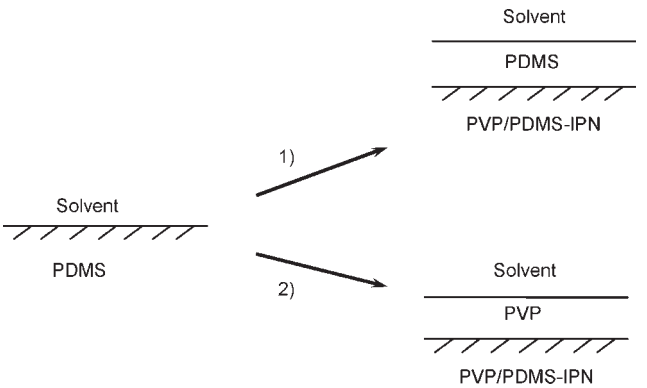

Figure 1 Illustration of the surface of the PVP/PDMS-IPN. Path 1 shows polymerization of NVP forming a PVP/PDMS-IPN in a solvent with $S < 0$ rendering a hydrophobic surface, while path 2 shows polymerization of NVP forming a PVP/PDMS-IPN in a solvent with $S \geq 0$ rendering a hydrophilic surface.

$$\gamma = \frac{m}{a} kT\chi \quad (4)$$

where *m* is a constant and denotes the fraction of nearest neighbors that are lost when a molecule is present at the surface compared with the bulk. *T* is the temperature in Kelvin, *k* is the Boltzmann constant, and *a* is the cross-sectional area per molecule. The χ-parameter indicates the compatibility between the components and is a measure of the ''antipathy'' of the components. The χ-parameter can be expressed in terms of the solubility parameter of the components using:

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + \beta \quad (5)$$

where V_1 is the molar volume of the solvent, *R* is the gas constant, and β is a constant, which expresses the entropic contribution. A normal value of β is 0.34.[18]

Equations (3), (4), and (5) can be combined as:

$$S = \frac{mkT}{a}\left[\frac{V_1}{RT}(\delta_{PDMS} - \delta_{Solvent})^2 + \beta_{PDMS/Solvent}\right] - \frac{mkT}{a}\left[\frac{V_1}{RT}(\delta_{PDMS} - \delta_{PVP})^2 + \beta_{PDMS/PVP}\right] - \frac{mkT}{a}\left[\frac{V_1}{RT}(\delta_{PVP} - \delta_{Solvent})^2 + \beta_{PVP/Solvent}\right] \quad (6)$$

To further simplify eq. (6) it is reasonable to assume $\beta_{PDMS/PVP} \approx 0$ due to the generally small entropy between two polymers, while on the other

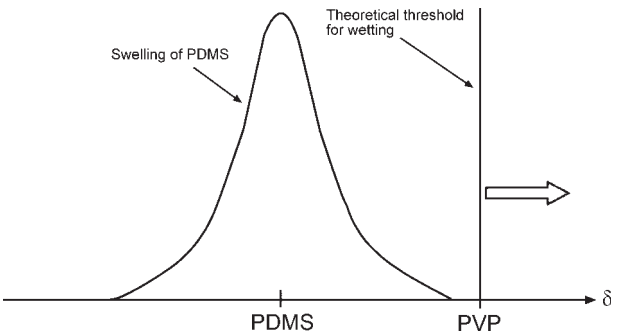

Figure 2 Schematic drawing of the requirements of the solvent to obtain a hydrophilic PVP/PDMS-IPN. First, the selected solvent has to be able to swell PDMS, which occurs for δ of the solvent close to PDMS. Second, the PVP film has to spread on PDMS, that is, $\delta_{Solvent} \geq \delta_{PVP}$ indicated by the arrow in the drawing.

hand $\beta_{PDMS/Solvent} \approx \beta_{PVP/Solvent}$. The latter assumption is valid for most polymer/solvent systems.[21,22] In the present system, the molar volume of the solvent is similar to the molar volume of the monomer, hence V_1 is similar for the PDMS/PVP-, PDMS/solvent- and PVP/solvent pairs. Hence, the expression in eq. (6) can be simplified to:

$$S = \frac{2mV_1}{aN_a}(\delta_{PDMS} - \delta_{PVP})(\delta_{PVP} - \delta_{Solvent}) \geq 0 \qquad (7)$$

where N_A is Avogadro's constant. Since we have already chosen our polymer system (PDMS and PVP) it is only the last factor in eq. (7) that can change the sign of the spreading coefficient. δ_{PDMS} and δ_{PVP} are constants and $\delta_{PDMS} < \delta_{PVP}$, thus $\delta_{Solvent} \geq \delta_{PVP}$ for the condition $S \geq 0$ to be valid. Hence, a model has been established for selecting solvent candidates to be able to polymerize a film at an interface of, that is, PVP and PDMS.

To obtain a hydrophilic PVP film at the PDMS surface, the solvents used in the preparation step should be close to, or larger than, the solubility parameter of PVP, that is, polar solvents must be used. The solvent should also dissolve the monomer, photoinitiator, and crosslinker. However, polar solvents will not be able to swell the elastomer and those with a solubility parameter close to PDMS are required. To fulfill these two requirements, a two-step method to obtain a PVP/PDMS-IPN is required. In the first step, the oil-soluble components (i.e., photointiator and crosslinker) are impregnated into the crosslinked PDMS using an efficient swelling solvent occurring at a solubility parameter close to that of the elastomer. In the second step, a solution containing the hydrophilic monomer is added. The solution should fulfill the requirement $\delta_{Solvent} \geq \delta_{PVP}$ to obtain a homogenous PVP-film at the PDMS surface. The reasoning for obtaining a hydrophilic PVP/PDMS-IPN is schematically presented in Figure 2.

Several PVP/PDMS-IPNs were investigated in the present study as outlined previously and the different solvents used for each step in the preparation are shown in Table I. The spreading coefficients, S, of different solvent combinations used in step 2 were calculated using eq. (7) and are listed in Table I. The systems investigated in this study have a large amount of NVP (up to 62 wt %) and, such large amount of NVP in the solution alters the total solubility parameter of the mixture.[22] Hence, a total solubility parameter taking into account the monomer (50 wt % NVP) and solvent in Step 2 was calculated (column 6, Table I). From the total solubility parameter the total spreading coefficient is calculated and is also included in Table I (column 7) and it should be compared with the spreading coefficient of the solvent (Table I, column 5).

Degree of polymerization in the PVP/PDMS-IPN

To determine the minimum time required for polymerization of the PVP/PDMS-IPN to occur, several samples were polymerized for different times. The times investigated were in the range 15–150 min as shown in Figure 3. It can be seen that no further increase in concentration of PVP in the PVP/PDMS-IPN occurs after 40 min.

Characterization of PVP/PDMS-IPN

The PVP/PDMS-IPN stability was tested following polymerization with respect to the leaching of non-crosslinked polymer by extracting in water until no further weight decrease was observed. The shelf-life of the samples was also investigated by initially stor-

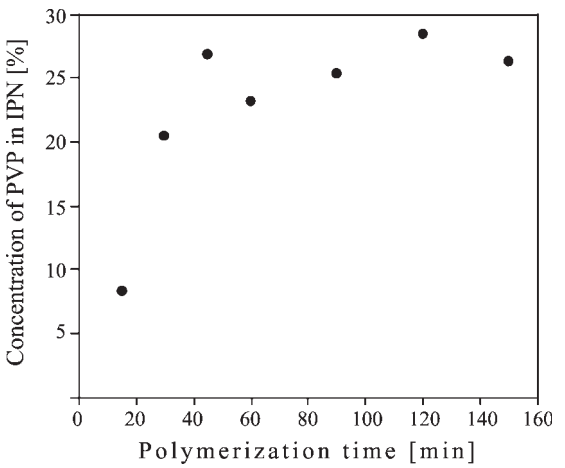

Figure 3 The concentration of PVP in the PVP/PDMS-IPN is plotted versus the time for polymerization for different samples. The monomer solution was 50 wt % NVP and 50 wt % solvent (30 wt % toluene and 70 wt % ethanol).

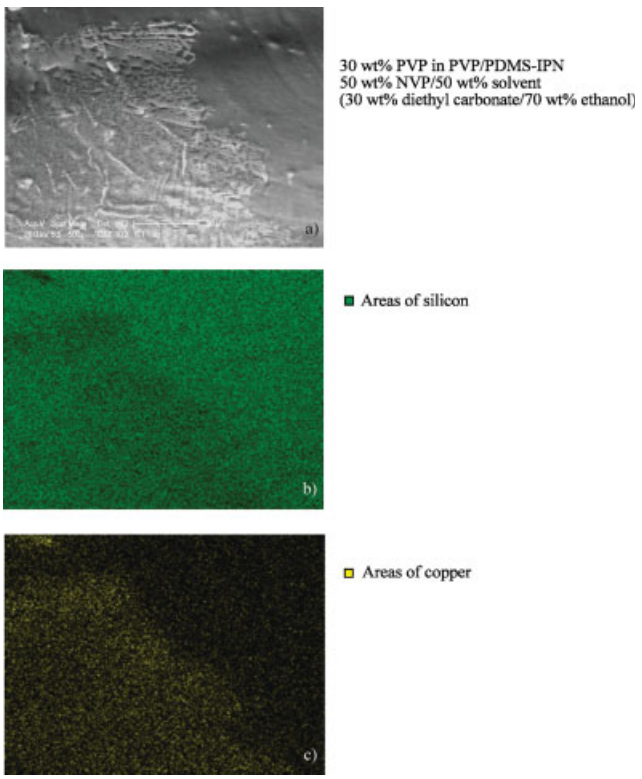

Figure 4 ESEM image of the cross section of the PVP/PDMS-IPN swollen in $CuSO_4$ (aq) is shown in (a). The elemental mapping of silicon and copper is shown in (b) and (c), respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing in water for 2 months after postpreparation, then the PVP/PDMS-IPN was dried out and the weight measured, followed by resoaking in water to measure the percentage water content of the samples. It was noted that the dry weight of the samples decreased by approximately 3 wt % and the swelling in water of the PVP/PDMS-IPN decreased by approximately 4 wt %. However, the hydrophilic PVP/PDMS-IPNs maintained its improved level of wettability after storage. For a number of applications, that is, in contact with the human body unwanted and nonspecific leaching of compounds from the substrate is unacceptable and inert IPN is desirable.

The main advantage of using a two-step method for preparation of a hydrophilic PVP/PDMS-IPN is that during the polymerization step, Irgacure 2100 and TEGDMA diffuse out of the crosslinked PDMS and simultaneously NVP migrates toward the polymer surface. This favors the formation of PVP at the interface and as polymerization occurs immediately following immersion into the monomer solution a hydrophilic PDMS surface is obtained. If the PDMS sample is soaked in monomer solution before initiating polymerization, this will only favor diffusion of Irgacure 2100 and TEGDMA into the outer monomer solution. As a result, the monomer solution will be polymerized to a larger degree outside PDMS and the final PVP/PDMS-IPN will contain less PVP. To confirm that the bulk of the PDMS contained PVP and an IPN had actually been formed, the samples were soaked in an aqueous solution of 0.1*M* copper sulfate ($CuSO_4$). This solution would only be able to penetrate the PDMS sample if hydrophilic PVP is present within the bulk. After soaking in $CuSO_4$ solution, PVP/PDMS-IPN samples were fractured in liquid nitrogen and the pieces were analyzed by ESEM and EDAX. The mapping of silicon (green) and copper (yellow) is shown in Figure 4 for a PVP/PDMS-IPN containing 30 wt % PVP. It can be seen that the elements are homogeneously distributed throughout the cross section confirming that PVP is present throughout the PDMS sample.

In general, wettability of the PVP/PDMS-IPN surfaces was characterized by simply withdrawing the sample from water and visually studying the spreading behavior of the liquid on the surface. Measuring the contact angle is the most sensitive and accurate method for determining surface wettability, as typically it is the outer molecular layers that affect the value. The spreading behavior of water on some selected PVP/PDMS-IPN surfaces is shown in Figure 5. The untreated PDMS clearly appears hydrophobic ($\theta = 93^\circ$) as do PVP/PDMS-IPNs with low content of PVP ($\theta = 91^\circ$). On the other hand, PVP/PDMS-IPNs with a high content of PVP result in a hydrophilic surface ($\theta < 20^\circ$) as evidenced by spreading of a water droplet on the surface. Therefore, from these results the PVP/PDMS-IPNs were characterized as hydrophilic.

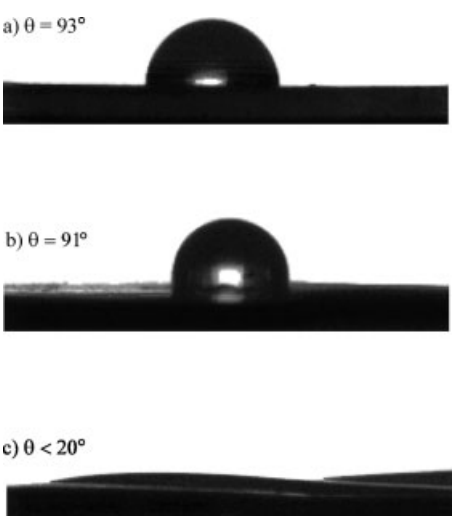

Figure 5 Images from contact angle measurements with water on (a) untreated PDMS; (b) 7.2 wt % PVP/PDMS-IPN, two step process (solvents: 30 wt % toluene/70 wt % ethanol), and (c) 44,0 wt % PVP/PDMS-IPN, two step process (solvents: 30 wt % toluene/70 wt % ethanol).

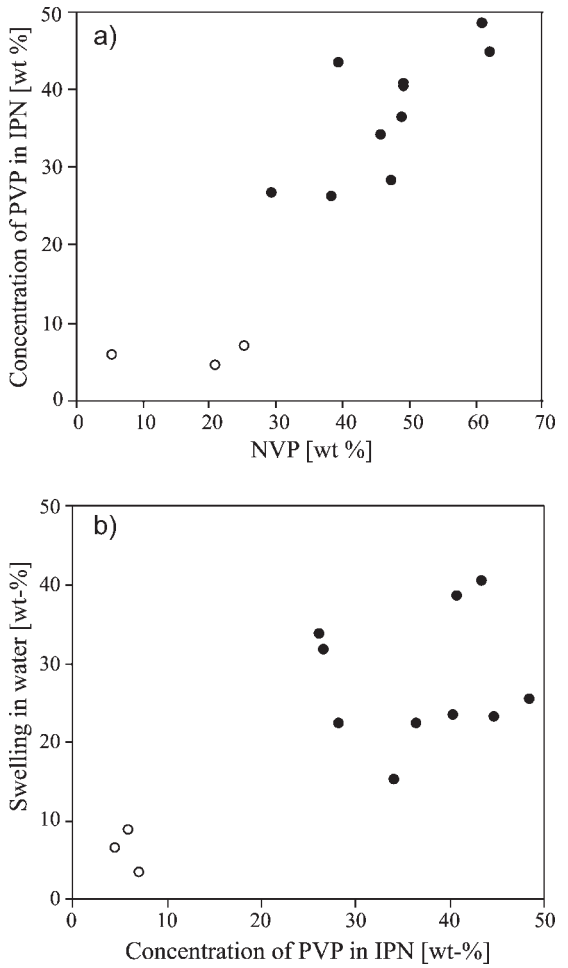

Figure 6 The concentration of PVP in the PVP/PDMS-IPN (polymerized in 30 wt % toluene/70 wt % ethanol) as a function of NVP concentration is shown in (a). The graph in (b) shows the swelling of PVP/PDMS-IPN in water as a function of concentration of PVP in the PVP/PDMS-IPN. The filled symbols represent hydrophilic PVP/PDMS-IPN and the open symbols represent hydrophobic PVP/PDMS-IPN.

All samples prepared in the present study using the two-step method were hydrophilic in nature as indicated in Table I. In Figure 6, samples were synthesized using toluene to swell the PDMS in the initial preparation step. In the second step, a mixture of toluene and ethanol was used as a solvent for the NVP. As can be seen in Figure 6(a), the PVP/PDMS-IPNs are hydrophilic above a certain threshold of NVP concentration, which is ~25 wt %. The observation can be explained by weak adhesive forces between PVP and PDMS and a sufficiently high PVP concentration in the PVP/PDMS-IPN is required to overcome them and to form a hydrophilic surface. This illustrates one of the challenges encountered when trying to synthesize a permanent hydrophilic PDMS surface. Increasing the NVP concentration has a marked effect on the PVP concentration in the final PVP/PDMS-IPN as shown in Figure 6(a). When the NVP concentration is increased up to 62 wt % the PVP concentration in the PVP/PDMS-IPN also increases. The concentration of PVP in the PVP/PDMS-IPN was calculated using eq. (1) following extraction of any monomer residues.

It was found that the IPN surfaces exhibit hydrophobic recovery if they are not stored in water following polymerization and this typically occurs within a few hours of removal from the solution. Therefore, the surfaces thus so far prepared in this study are not permanently hydrophilic under ambient conditions. Samples that have been stored in air for 1 month and then reimmersed in water will become hydrophilic within 1 h. When the samples are kept in air, the low molecular weight species in PDMS migrate toward the air surface to lower the surface energy and hence, the PVP/PDMS-IPN turns hydrophobic. This tendency for the low molecular species in PDMS to migrate out toward the surface is well known and has been described by Vickers et al.[23] It is also possible that a segment of the PDMS backbone will rearrange in air and hence methyl groups will reorientate towards the surface. Even though all the low molecular weight species are thought to be extracted from PDMS the surface will still be able to rearrange when in contact with air to minimize the interfacial free energy.[24] This shows that hydrophobic recovery on the surface of the PVP/PDMS-IPNs investigated in this study can be prevented if the samples are stored in water. Although this will limit the overall use of the PVP/PDMS-IPNs, a number of biomaterials are continuously in contact with water, such as contact lenses and implantable devices, where IPNs prepared by the two-step method is an interesting alternative.

The swelling of the PVP/PDMS-IPN in water was measured using eq. (2) and is illustrated in Figure 6(b). The data shows some scattering, however, there is an increasing trend for increasing of swelling with concentration of PVP in the IPN and therefore it is assumed that the swelling correlates with the fraction of PVP in the PVP/PDMS-IPN. It is most likely also dependent on the degree of crosslinking.[25] Other parameters, such as concentration of photoinitiator may also have an effect during the preparation procedure of the IPN. The concentration of photoinitiator will affect the molecular weight of the polymer and this will in turn affect the swelling in water of the PVP/PDMS-IPN.

As previously described, for comparison with the two-step method, some samples were prepared by mixing all components in a one step process. The solvents used were cyclohexane, ethanol, toluene, and a mixture of toluene and ethanol (30/70 wt %). Hydrophobic samples were obtained and the result-

ing concentration of PVP found in the PVP/PDMS-IPN was much lower than with the two-step method. Generally, the concentration of PVP found in the IPNs was no higher than 10 wt % using the one step method. This further supports the theory that there is a limiting PVP concentration (~25 wt %) in the PVP/PDMS-IPN below which it appears to be impossible to obtain a hydrophilic surface [see Fig. 6(a)]. Using the one-step method, the limiting PVP concentration in the IPN was not achieved and the samples remained hydrophobic in nature. This illustrates the validity of a two-step method for the preparation of a hydrophilic PVP/PDMS-IPN regardless of which solvents are used during preparation.

From the summary in Table I, it can be concluded that many different solvent combinations allow a hydrophilic PVP/PDMS-IPN to be prepared, some using either toluene or ethanol in the second step and resulting in a water wettable surface. Other samples were prepared using water saturated with toluene, to prevent toluene in the swollen PDMS from diffusing out into the solution, in the second step and a hydrophilic PVP/PDMS-IPN resulted. Hydrophilic PVP/PDMS-IPNs were obtained when diethyl carbonate, cyclohexane, or *n*-hexane were used in the first step, followed by diethyl carbonate/cyclohexane/*n*-hexane with ethanol in the second step. Additionally, PVP/PDMS-IPNs were prepared using cyclohexane or *n*-hexane in the second step. The samples turned hydrophilic, although calculations of the spreading coefficient, S, for cyclohexane and *n*-hexane indicated that the surface of the PVP/PDMS-IPN should remain hydrophobic using such solvent combinations. These findings appear contradictory, but one explanation might be that the system is not at equilibrium during the polymerization. Nonequilibrium conditions can result for high monomer and photoinitiator concentrations when the polymerization rate is high. Even though there is less NVP at the PDMS surface using nonpolar solvents, the PVP chains that are formed at the PDMS surface will attract more NVP as the polymerization progresses. Hence, any deficiency of NVP will shift to an excess at the surface and the polymerization rate will be accelerated. The NVP/solvent compositions at a PDMS surface and a PVP surface were calculated. The calculations were performed using the regular solution theory and χ-parameters for the different components in the system were inserted into eq. (10) in Ref. [26] to calculate the NVP/solvent composition at the surface of the substrate and the bulk of the solution.[26] It was found that for a 50/50 wt % NVP/solvent mixture the NVP concentration is 25 wt % at the PDMS surface, whereas it is 60 wt % at the PVP surface. These figures support the theory outlined above.

CONCLUSIONS

It is possible to prepare hydrophilic PVP/PDMS-IPNs by using a two-step method. In the first preparation step, the PDMS sample is soaked in a solvent with sufficient ability to swell PDMS and solubility for NVP and PVP to impregnate crosslinker and photoinitiator. In the second step, the preimpregnated PDMS is soaked in a monomer solution and polymerization is carried out. PVP/PDMS-IPNs having surfaces which displayed complete spreading of a water droplet were obtained if the NVP concentration was held above a certain threshold (~25 wt % NVP). The theoretical considerations discussed in this work suggest that the choice of solvent in the second step is critically important for obtaining a hydrophilic surface. This was not confirmed during these experiments as all solvents gave hydrophilic surfaces provided that the NVP concentration was above the threshold value. PVP/PDMS-IPNs prepared using the two-step method were compared with a one-step procedure, where the PDMS sample was immersed with all chemicals simultaneously followed by subsequent UV-curing. These samples remained hydrophobic even following immersion and storage in water. This further supports the rationale for using a two-step method to obtain a hydrophilic PVP/PDMS-IPN. It is proposed that the methodology developed within this study can be used for combining other incompatible polymer pairs by forming suitable IPN materials where combining properties from different polymer are of interest.

Dr. Joachim Karthäuser at Linde Gas/AGA AB is thanked for presenting the project and for stimulating discussions. Dr. Kathryn J. Kitching is thanked for her assistance with the preparation of this manuscript.

References

1. Noll, W. Chemistry and Technology of Silicones; Academic Press: New York, 1968.
2. Skeist, I. In Handbook of Adhesives; Skeist, I.; Miron, J., Eds.; Van Nostrand Reinhold: New York, 1990; p 13.
3. LaPorte, R. J. Hydrophilic Polymer Coatings for Medical Devices—Structure/Properties, Development, Manufacture and Applications; Technomic Publishing Company Inc.: Basel, 1997.
4. Abbasi, F.; Mirzadeh, H.; Katbab, A.-A. Polym Int 2001, 50, 1279.
5. Inagaki, N. Plasma Surface Modification and Plasma Polymerization; Technomic Publishing Company, Inc.: Pennsylvania, 1996.
6. Lawrence, J.; Li, L. Laser Modification of the Wettability Characteristics of Engineering Materials; Professional Engineering Publishing Limited: Suffolk, 2001.
7. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer—Polymer Miscibility; Academic Press: New York, 1979.

8. Sperling, L. H. Interpenetrating Polymer Networks and Related Materials; Plenum Press: New York, 1981.
9. Abbasi, F.; Mirzadeh, H. Int J Adhesion Adhesives 2004, 24, 247.
10. Liu, L.; Sheardown, H. Biomaterials 2005, 26, 233.
11. Erbil, C.; Kazancioglu, E.; Uyanik, N. Eur Polym Mater 2004, 40, 1145.
12. Barabas, E. S. In Encyclopedia of Polymer Science and Engineering; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1989; Vol 17, p 198.
13. Refojo, M. F. In Kirk-Othmer Encyclopedia of Chem Technology, 3rd Edition; Kirk, R. E.; Othmer, D. F., Eds.; Wiley: New York, 1984; Vol 6, p 720.
14. Cifkova, I.; Lopour, P.; Vondracek, P.; Jelinek, F. Biomaterials 1990, 11, 393.
15. Shin, M.-S.; Kim, S. J.; Kim, I. Y.; Kim, N. G.; Song, C. G.; Kim, S. I. J Appl Polym Sci 2002, 85, 957.
16. Barton, A. CRC Handbook of Solubility Parameters and other Cohesion Parameters, second edition; CRC Press: Florida, 1991.
17. Mark, J. E. Physical Properties of Polymers Handbook; Americans Institute of Physics: Woodbury, 1996.
18. Brandrup, J.; Immergut, E. Polymer Handbook, Third Edition; Wiley: New York, 1989.
19. Horak, D.; Krystufek, M.; Spevacek, J. J Polym Sci Part A: Polym Chem 2000, 38, 653.
20. Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B. Surfactants and Polymers in Aqueous Solution; Wiley: West Sussex, 2003.
21. Hildebrand, J. H.; Scott, R. L. The Solubility of Nonelectrolytes; Dover Publications, Inc.: New York, 1964.
22. Blanks, R. F.; Prausnitz, J. M. Ind Eng Chem Fundamentals 1964, 3, 1.
23. Vickers, J. A.; Caulum, M. M.; Henry, C. S. Anal Chem 2006, 78, 7446.
24. Chen, C.; Wang, J.; Chen, Z. Langmuir 2004, 20, 10186.
25. Abbasi, F.; Mirzadeh, H. J Polym Sci Part B: Polym Phys 2003, 41, 2145.
26. Kronberg, B. J Colloid Interface Sci 1983, 96, 55.