

Transparency and Wettability of PVP/PDMS-IPN Synthesized in Different Organic Solvents

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ABSTRACT: An interpenetrating polymer network (IPN) combining a hydrophobic polymer (polydimethylsiloxane, PDMS) and a hydrophilic polymer (polyvinylpyrrolidone, PVP) was synthesized in different solvents via a two-step preparation method. The solvent used during polymerization of the IPN showed a significant impact on the properties of the PVP/PDMS-IPN. The choice of solvent was affecting both the wettability and transparency of the PVP/PDMS-IPN. The PVP/PDMS-IPNs turned hydrophilic in all the solvents used in this study, but the transition from a hydrophobic to a hydrophilic PVP/PDMS-IPN occurred at lower PVP concentration if a solvent with similar solubility parameter as PVP was chosen. Also, the PVP/PDMS-IPNs

were transparent when the samples were polymerized in a good solvent for PVP. It was concluded that the properties of the PVP/PDMS-IPN can be tuned by the selection of the solvent used during polymerization. The size of the PVP phase domains in the PVP/PDMS-IPNs were analyzed with X-ray scattering techniques (SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC), and the sizes of the domains were found to be smaller than 350 nm. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1828–1839, 2009

Key words: interpenetrating polymer networks; silicones; hydrogels; phase separation; transparency

INTRODUCTION

Considerable attention has been given to systems where different types of polymers are combined, aiming at improving the material properties of the polymer without the need of synthesizing a totally new polymer. Generally, different types of polymers are not miscible and they tend to show a large degree of phase separation if they are blended. A special case of polymer blends are interpenetrating polymer networks (IPNs), which can be synthesized by a manifold of preparation methods. The common feature of IPNs is that at least one of the polymers is in network form, held together by mutual entanglements of the polymer chains. In comparison with polymer blends, an IPN tends to show a lower degree of phase separation because of these forced entanglements.¹ This affects the mechanical properties of the material as well as the morphology of the

IPN, which is very important for biocompatibility, mass transfer through the material, optical properties, and permeability of the IPN.^{2–4} Several authors have investigated the morphology in IPNs with different microscopy techniques.^{5–8} Most commonly, scanning electron microscopy (SEM) or transmission electron microscopy (TEM) have been used for analyzing the phase separation in the IPNs, but also confocal laser scanning microscopy (CLSM) has been used to visualize the morphology of IPNs.

Although the literature treating IPNs is extensive, the majority of the studies are focusing on the mechanical properties of the IPNs.^{9–11} In many cases, not only the mechanical properties of polymer materials but also their physical appearance and surface properties are of interest for a particular application. For such applications, combining hydrophobic–hydrophilic polymer pairs are very challenging both from a scientific viewpoint, as well as for commercial products. Reports on the preparation of IPNs based on hydrophobic polydimethylsiloxane (PDMS) and another hydrophilic polymer are frequent.^{2,4,12–14} Synthesizing an IPN of incompatible polymers offers an advantage in comparison with forming a polymer blend because the degree of phase separation is lower in an IPN.

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Here, we describe the synthesis of an IPN containing two highly incompatible polymers, where the properties of the IPN can be tuned by the selection of solvent used in the synthesis. The hydrophobic polymer is PDMS, whereas the hydrophilic polymer is polyvinylpyrrolidone (PVP). When PVP is cross-linked, it forms a hydrogel which efficiently swells in water and has excellent biocompatibility.¹⁵ In a previous report, we have demonstrated a novel preparation method for the synthesis of hydrophilic PVP/PDMS-IPN. This method is also used in this study, but the aim is to gain a deeper understanding on the selection of solvent used for the polymerization of the PVP/PDMS-IPN.¹⁶ The preparation method for the synthesis of the IPN is affecting both the surface and bulk properties of the PDMS. The surface property that is investigated is the wettability by water of the surface of the PVP/PDMS-IPN, which is very important for many biomedical applications, such as for catheters and contact lenses, where the material will be in contact with body fluids. The pure PDMS shows no wettability toward water, but when a PVP/PDMS-IPN is formed, consisting of PDMS and a hydrophilic polymer, the surface becomes hydrophilic.

In addition, the bulk property that is investigated is the optical transparency of the material, since a high transparency is crucial for some applications, e.g., contact lenses. The transparency of the material is also intimately related to the degree of miscibility between the polymers, and this study aims at determining the degree of phase separation in the IPN. In general, the physical properties of IPN are highly dependent on the morphology because of phase separation. In this study, the phase domains of the IPNs are analyzed with TEM, SEM, and X-ray scattering techniques. Also, differential scanning calorimetry (DSC) has been used as it is a well-established method to measure the compatibility in IPNs. Combining these results with the results of the physical characteristics of the IPN, in terms of wettability and transparency, yields a deeper understanding of solvent effects during polymerization of IPNs.

EXPERIMENTAL

Materials and methods

The PDMS elastomer sheeting was supplied by Mentor Corporation (The Netherlands) and was 0.51-mm thick and has 50 Shore A hardness. The hydrophilic monomer was *N*-vinyl-2-pyrrolidone (NVP), stabilized with 0.01% NaOH (Aldrich, Germany). The crosslinker was triethyleneglycol dimethacrylate, TEGDMA, stabilized with approximately 80 ppm hydroquinone (95%, Aldrich) and the photoinitiator was Irgacure 2100, which is a mixture of mono- and

bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Ciba Speciality Chemicals, Switzerland). The solvents used for the swelling of PDMS and polymerization of the PVP/PDMS-IPN were *n*-hexane (p.a, Merck, Germany), cyclohexane (p.a, Merck), diethyl carbonate (99%, Aldrich), toluene (p.a, Merck), 1-propanol (p.a, Merck), 2-propanol (p.a, Merck), and di(ethylene glycol)ethyl ether (99+%, Sigma-Aldrich, Germany). All materials were used as received.

The detailed experimental procedure to prepare the PVP/PDMS-IPN is described elsewhere.¹⁶ In brief, the synthesis is divided into the following steps: (1) swelling of PDMS to load the oil-soluble components (the photoinitiator and the crosslinker), (2) immersion of the swollen PDMS in a second solution containing monomer and solvent followed by UV-initiation of the polymerization reaction in the solution. For each solvent used for polymerization of the PVP/PDMS-IPNs, various monomer concentrations in the solution were used, in the concentration range between 5 and 66%. The solvents in Steps 1 and 2 were the same and they have been varied systematically. Finally, residues from the polymerization process were extracted from the PVP/PDMS-IPN by immersing it in water. The samples were stored in water as this turns out to ensure a hydrophilic surface if the samples were water wettable.

The free-radical polymerization of the PVP/PDMS-IPN was initiated by a mercury-xenon lamp (200W, LC-8 model L8868-02, Hamamatsu, Japan), and the PDMS sample and the solution was exposed for UV light for at least 60 min to ensure a fully polymerized PVP/PDMS-IPN. The UV-intensity was measured with a light power meter at 365 nm (model C6080-03, Hamamatsu, Japan), and the UV-intensity was constant at 300 mW/cm² during the whole reaction. All experiments were carried out at ambient temperature.

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

The concentration of PVP in the PVP/PDMS-IPN was calculated from dry weights after water extraction from residues in the PVP/PDMS-IPN:

$$\% \text{PVP} = \left(\frac{w_d - w_0}{w_d} \right) \times 100 \quad (1)$$

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.

The swelling in water was measured by immersion of a dry PVP/PDMS-IPN of known weight in an excess amount of distilled water at ambient temperature. The PVP/PDMS-IPN was left in the water for 24 h before blotting the PVP/PDMS-IPN between two

sheets of dust-free tissue paper, and the water uptake of the PVP/PDMS-IPN was calculated as follows:

$$\% \text{ Swelling in water} = \left(\frac{w_s - w_d}{w_d} \right) \times 100 \quad (2)$$

where w_s is the weight of the PVP/PDMS-IPN after swelling in water. The PVP percentage and the water content percentage were calculated on weight basis and are hereafter denoted as %.

Contact angle measurements

The hydrophilicity of the surface of the PVP/PDMS-IPN was characterized by withdrawing the swollen samples from water and visually observing the wetting behavior of the water film on the surface. A hydrophilic PVP/PDMS-IPN showed total spreading of the water film on the surface. If the water film formed droplets on the surface it was defined as a hydrophobic PVP/PDMS-IPN.

Transparency measurements

The transparency of the PVP/PDMS-IPN was measured using a UV/vis spectrophotometer (UVLambda 650, Perkin-Elmer, USA). The transmittance of PVP/PDMS-IPN swollen in water was measured at a wavelength of 550 nm by placing the sample in front of the beam. The transparency was calculated as follows:

$$\% \text{ Transparency} = \left(\frac{\% \text{ Transmittance IPN}}{\% \text{ Transmittance PDMS}} \right) \times 100 \quad (3)$$

For each sample, the transmittance was measured at three different positions on the sample, and the mean value and standard error of the mean was used to calculate the transparency for each sample.

Small-angle X-ray scattering

The small-angle X-ray scattering (SAXS) data of PVP/PDMS-IPNs swollen in water were obtained with a modified version of the Nanostar SAXS equipment (produced by Anton Parr, Austria, and distributed by Bruker AXS, Germany). The experiments were performed in the standard setup (67 cm from the sample to the detector distance) with a rotating Cu $K\alpha$ anode. The data were collected by a HiSTAR (Bruker AXS) two-dimensional position-sensitive detector (1024 \times 1024 pixels). Thin slices of the samples were cut and placed in a thermostated quartz capillary and subsequently swollen with water by filling the capillary by water. Measurements were performed in the range of scattering vectors [$q = (4\pi/\lambda) \sin\theta$] from 0.01 to 0.35 \AA^{-1} , where 2θ is the scattering angle and λ is the wavelength].

Transmission electron microscopy

PVP/PDMS-IPN and PDMS samples exposed to water were rapidly frozen in liquid propane and transferred to Balzer BAF 400 Freeze Etching System (Balzers AG, Lichtenstein). Because of the rapid cooling in the chamber, only amorphous ice was formed and the ice was thereafter sublimated. The samples were fractured at -100°C for PVP/PDMS-IPN and at -130°C for the PDMS. Different temperatures were used because it was not possible to fracture PDMS at a higher temperature. Both materials swollen in water were etched at -100°C for 5 min. To obtain the replica, the etched surfaces were rotary shadowed with Pt/C at an angle of 45° and C at an angle of 80° . The thickness of the Pt/C layer was checked with a quartz crystal monitor. The replicas were cleaned in distilled water, methanol (only IPN), chloroform, xylene (only IPN), warm NaOH, room-temperature NaOH, and finally with distilled water and mounted on copper 400 mesh grids. The samples were analyzed with a TEM (LEO 906E, LEO Elektronmikroskopie, Germany) at an accelerating voltage of 80 kV. Images were recorded by a slow-scan CCD camera Proscan HSC2.

Scanning electron microscopy

A SEM fitted with an energy dispersive X-ray spectrometer (EDAX; XL30 ESEM TMP, FEI/Philips, The Netherlands) was used to analyze dry cross sections of PDMS and PVP/PDMS-IPNs. The electron acceleration voltage was 15 kV, and the images were recorded at 5000 \times magnification. The microscope was operated in low vacuum mode when images were obtained with the backscattering detector (BSE), and it was operated in high vacuum mode when images were obtained with the secondary electron detector (SE). The samples analyzed with the SE detector were coated with a gold layer of ~ 450 \AA thickness using a sputter coater (SCD 050, Baltzers Union AG, Lichtenstein). The thickness of the gold layer was derived from the operating instructions for the sputter coater. The size of the phase domains of the PVP/PDMS-IPN from the SEM images were calculated using the ImageJ program (National Institutes of Health, USA).

Differential scanning calorimetry

The glass transition temperature of PDMS of the pure starting material as well as PVP/PDMS-IPNs polymerized in 1-propanol or cyclohexane were measured with a DSC (DSC1, Mettler-Toledo, Switzerland) equipped with liquid nitrogen cooling unit. Before the measurement, the temperature axis of the DSC was calibrated with three different standards: indium (melting point, $M_p = 156^\circ\text{C}$), *n*-octane ($M_p = -56^\circ\text{C}$),

and *n*-hexane ($M_p = -95^\circ\text{C}$). All samples (8–13 mg) were submitted to the same temperature scan, which consisted of cooling the DSC to -140°C and then inserting the sample into the DSC furnace. The sample was then isothermally stabilized at -140°C for 3 min and then heated with a scanning rate of $10^\circ\text{C}/\text{min}$ up to 200°C . During the measurements, a continuous N_2 purge at 50 mL/min was used.

RESULTS AND DISCUSSION

Several PVP/PDMS-IPNs were synthesized according to the preparation method described in the Experimental section. The preswelling and subsequent polymerization of PVP/PDMS-IPN were performed in solvents with a range of solubility parameters, δ , see Table I. In our previous study, it was concluded that to synthesize a hydrophilic PVP/PDMS-IPN, the solvent used during the polymerization needs to fulfill two requirements: (1) it should swell PDMS to load the components for the free-radical polymerization and (2) it should facilitate PVP to form a wetting film on the PDMS surface after polymerization of the PVP/PDMS-IPN. The first condition can be fulfilled by selecting a nonpolar solvent, which easily swells PDMS. On the other hand, obtaining a wetting PVP film after polymerization of the IPN can only be achieved if there is an excess of PVP on the surface, otherwise it will remain hydrophobic. A PVP film can only spread on PDMS if there is an energy gain, i.e., the total surface energy is lower after polymerization of the IPN.¹⁶

Swelling of PDMS in solvents and obtained PVP concentration in the IPN

The effect of the solubility parameter of the solvent for swelling of PDMS is seen in Table I. As can be seen from the table, the less polar solvents, such as

toluene, diethyl carbonate, cyclohexane, and *n*-hexane, swell the PDMS substantially more than the more polar solvents, such as 1-propanol, 2-propanol, and di(ethyleneglycol)ethyl ether. These results could be expected, as it is well known that the most substantial swelling of a given polymer is obtained when the solubility parameter of the solvent and that of the polymer are similar. PDMS has a solubility parameter of $14.9 \text{ MPa}^{1/2}$, which is close to the solubility parameters of the nonpolar solvents, and it swelled PDMS to a great extent.¹⁷

Of all evaluated solvents, hexane is one of the most efficient swelling solvent for PDMS, whereas 1-propanol shows a poor swelling ability (see Table I). As a consequence of these differences in swelling behavior, the obtained concentration of PVP in the PVP/PDMS-IPNs was higher in samples polymerized in nonpolar solvents like hexane when compared with samples for which the polymerization took place in the more polar solvents, like 1-propanol. The effect is most likely due to the presence of a higher amount of monomer (and crosslinker and initiator) in the PDMS during polymerization in the hydrophobic, more PDMS-swelling solvents.

Wettability of the PVP/PDMS-IPN

As noted earlier, a nonpolar solvent is optimal for incorporating a large amount of PVP into the PDMS matrix. However, the samples polymerized in more polar solvents, having solubility parameters close to PVP and NVP ($\delta_{\text{PVP}} = 23.3 \text{ MPa}^{1/2}$ and $\delta_{\text{NVP}} = 21.5 \text{ MPa}^{1/2}$)^{17,20} gave hydrophilic IPNs already at much lower PVP contents in the IPNs when compared with IPNs synthesized in nonpolar solvents. This effect can be observed in Table II where the percentage of PVP needed to render hydrophilic IPN is presented. As can be seen from the table, PVP/PDMS-IPNs polymerized in 1-propanol become hydrophilic

TABLE I
Summary of the Results of Polymerizing PVP/PDMS-IPNs in a Solution Containing 50% NVP

Solvent	Degree of swelling in PDMS (%)	δ ($\text{MPa}^{1/2}$) ^{17,25,26}	Conc. PVP in IPN (%)	Transparency of IPN (%)	Number of samples
1-Propanol	11	24.3	18.2 ± 2.5	73.0 ± 21.3	3
2-Propanol	15	23.5	17.5 ± 1.3	70.2 ± 29.6	3
Di(ethylene glycol) ethyl ether	2	21.9	9.7 ± 0.7	123.8 ± 5.3	3
Toluene	125	18.2	27.0 ± 5.0	47.8 ± 15.2	5
Diethyl carbonate	48	18.0	28.2 ± 3.1	41.9 ± 19.6	2
Cyclohexane	126	16.8	36.2 ± 9.1	5.3 ± 6.0^b	5
<i>n</i> -Hexane ^a	101	14.9	32.8 ± 9.7	0.6 ± 0.9^b	5

The degree of swelling refers to swelling of PDMS in pure solvent. All samples showed wettability.

$\delta_{\text{PDMS}} = 14.9 \text{ MPa}^{1/2}$; $\delta_{\text{PVP}} = 23.3 \text{ MPa}^{1/2}$; $\delta_{\text{NVP}} = 21.5 \text{ MPa}^{1/2}$.

^a The solubility limit of NVP in hexane is 15%.

^b The samples were highly cured after polymerization.

TABLE II
Concentration of the Monomer and the Corresponding PVP Concentration for the Transition from a Hydrophobic to a Hydrophilic PVP/PDMS-IPN for the Different Solvents

Solvent	Conc. NVP (%)	Conc. PVP in IPN (%)
1-Propanol	20–30	15
Toluene	40–50	22
Diethyl carbonate	30–40	26
Cyclohexane	20–30	30
n-Hexane	50–52	52

at a much lower concentration of PVP in the PVP/PDMS-IPN than samples polymerized in a nonpolar solvent like hexane. The effect is in accordance with our findings in a previous report where it was concluded that polar solvents are ideal for obtaining hydrophilic IPNs.¹⁶

Swelling in water

The swelling behavior of PVP/PDMS-IPNs polymerized in different solvents is summarized in Figure 1. As can be seen from the figure, the swelling of PVP/PDMS-IPNs in water increases linearly with increasing concentration of PVP in the PVP/PDMS-IPNs. Because PVP is a hydrogel,^{15,21} it is natural that the IPNs swell in proportion to their PVP content.

The data in Figure 1 for the IPNs polymerized in hexane shows much scattering. One possible explanation for this is that NVP was not fully soluble in hexane. The solubility limit of NVP in hexane is 15%, however, the experiments were conducted also above this limit, using two-phase dispersions containing up to 66% NVP in hexane. The reproducibility of this particular experiment was low, probably due to poor control of the NVP amount entering the PDMS via the two-phase system. Note that the reproducibility was not a problem at low NVP concentrations. PVP/PDMS-IPNs, with a low amount of PVP (produced with hexane solutions of NVP, with a concentration below the 15% solubility limit) can be seen to fit well to the general linear correlation reported in Figure 1. For all other solvents than hexane used in this study, the monomers were completely soluble.

It should be noted that for all solvents, the PVP/PDMS-IPNs that remained hydrophobic (meaning that a water film on the sample in air spontaneously formed droplets with a measurable contact angle) also did swell in water to a certain degree.

Storage stability of PVP/PDMS-IPN

In addition to determine the wettability in the PVP/PDMS-IPN, the storage stability of PVP/PDMS-IPNs has been investigated. It was shown that these materi-

als remained hydrophilic as long as they were stored in an aqueous solution. In dry state, the hydrophilic PVP/PDMS-IPNs turned hydrophobic. However, this effect was reversible and as soon as they were placed in water they turned hydrophilic within an hour.

Another important aspect regarding stability, if the goal is to use the PVP/PDMS-IPN in biomedical applications, is that no significant weight loss should be observed when the PVP/PDMS-IPNs are stored in water; oligomers of any kind may not be leached out from the IPN during usage of the material. Therefore, the weight loss of the PVP/PDMS-IPNs after 2 months of storage in water was investigated, and it was found that the material retains its hydrophilic properties after this time period, even though a small (ca. 2 %) decrease of the PVP concentration in the PVP/PDMS-IPN could be observed for some samples. In general, if the concentration of PVP in the PVP/PDMS-IPN decreased slightly after 2 months of storage, also the swelling in the PVP/PDMS-IPN decreased to the same extent, which is in full agreement with the correlation found in Figure 1, and also verifies that the lost material (found by gravimetric analysis) was indeed PVP.

Transparency

Figure 2(a,e) shows the transparency as the PVP concentration in the PVP/PDMS-IPN is increased. The

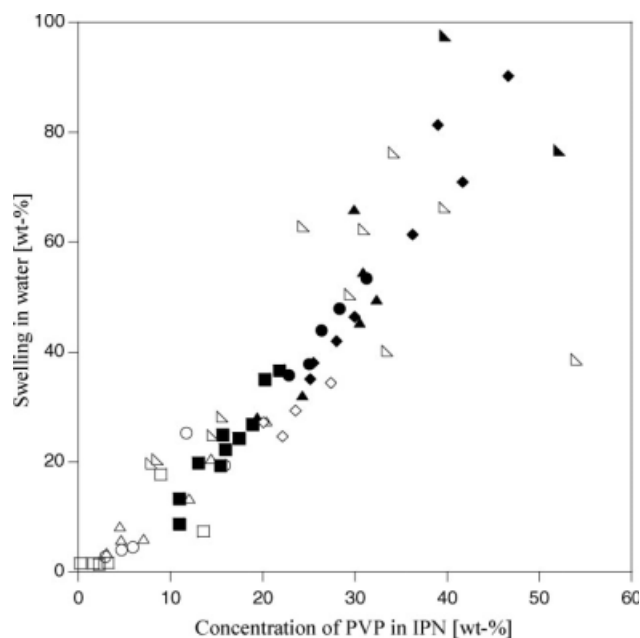


Figure 1 Relationship between concentration of PVP and the swelling in water of the PVP/PDMS-IPNs polymerized in five different solvents. The symbols are corresponding to ■ = 1-propanol, ▲ = toluene, ● = diethyl carbonate, ◆ = cyclohexane, and ▼ = hexane. The filled symbols indicate the hydrophilic samples and the unfilled symbols indicate the hydrophobic samples.

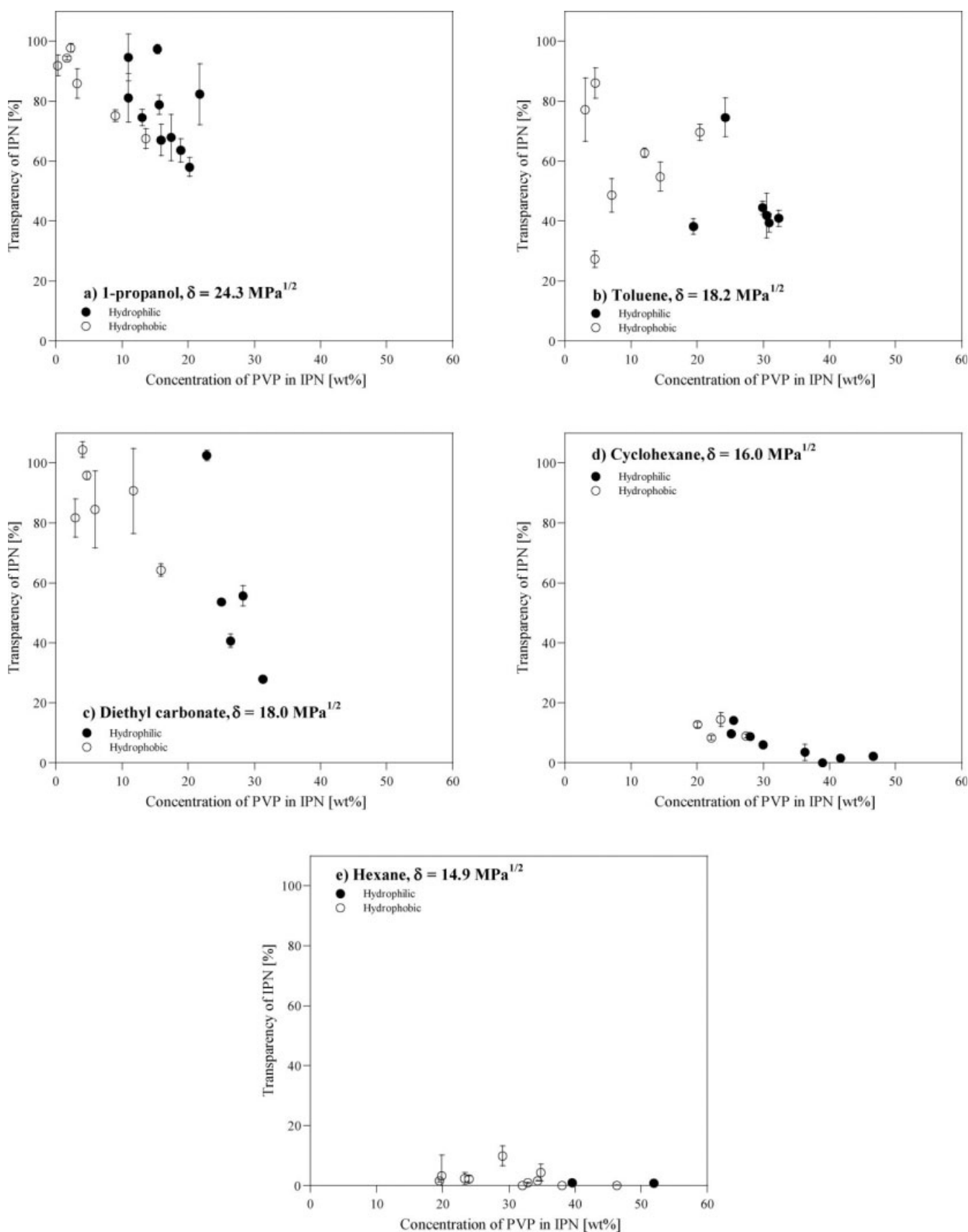


Figure 2 The transparency of the material versus concentration of PVP in PVP/PDMS-IPN after swelling in water. The error bar is the standard error of the mean calculated for three measurements.

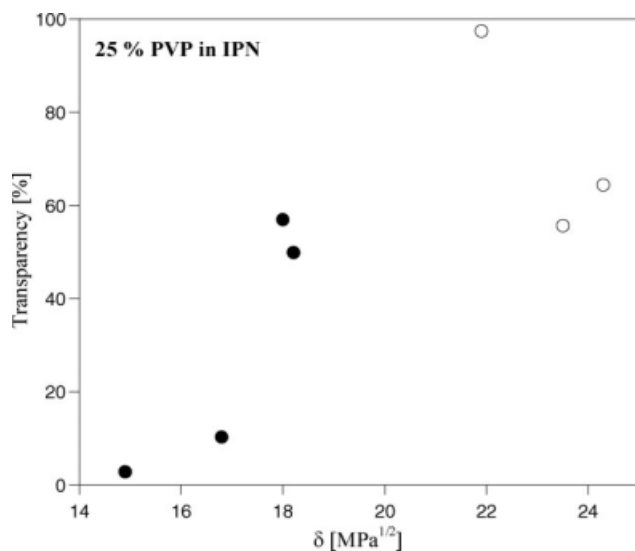


Figure 3 The transparency of the PVP/PDMS-IPN is increased as the solubility parameter of the solvent is increased, i.e., when a more polar solvent is used for polymerization of the IPN. The values were obtained by interpolating the transparency data at 25% PVP in the PVP/PDMS-IPN (filled symbols) or by extrapolating to 25% PVP in the PVP/PDMS-IPN (unfilled symbols).

transparency of the PVP/PDMS-IPN was measured after swelling in water. As can be seen, the solvent has a significant influence on the transparency of the PVP/PDMS-IPN. IPNs polymerized in 1-propanol showed high transparency, but it decreased as the concentration of PVP in the IPN is increased. When polymerizing PVP/PDMS-IPN using solvents with a lower solubility parameter (toluene, diethyl carbonate, cyclohexane, or hexane) than that of 1-propanol, the transparency of the PVP/PDMS-IPN was found to be lower. PVP/PDMS-IPNs polymerized in cyclohexane or hexane had only a transparency of approximately 10% (or lower, as the concentration of PVP in the PVP/PDMS-IPN was increased).

In Table I, where the results are summarized for PVP/PDMS-IPNs polymerized in a monomer solution containing 50% NVP, two additional solvents have been tested to find a solvent that would form a hydrophilic and transparent PVP/PDMS-IPN. Using di(ethylene glycol)ethyl ether as the polymerization medium resulted in PVP/PDMS-IPNs which were highly transparent (124%, i.e., even higher than for the PDMS reference) and also hydrophilic. PDMS swells only to a small degree in this solvent (2%) but the swelling is obviously still sufficient to load the PDMS matrix with enough initiator (and crosslinker) for initiation of the polymerization reaction. The second solvent, 2-propanol, formed hydrophilic PVP/PDMS-IPNs, but the transparency was only 70% in comparison with pure PDMS.

These results are also summarized in Figure 3 showing that transparency of the PVP/PDMS-IPN

was high when a more polar solvent was used during polymerization. The data in the graph were obtained by interpolating or extrapolating to a transparency of 25% PVP in the PVP/PDMS-IPN for the different solvents. The scattering of the data in the graph does not allow us to conclude whether or not there is a maximum in the graph but there is a tendency that di(ethyleneglycol)ethylether (at $\delta = 21.9$ MPa^{1/2}) is the most favorable solvent to use because of its high transparency and wettability with water of the PVP/PDMS-IPN.

The need for a good solvent during polymerization of the PVP/PDMS-IPN is also important from another aspect, as already has been discussed in the section about the wettability of the PVP/PDMS-IPN. One should use a good solvent for PVP (with a solubility parameter similar to that of PVP) to facilitate the formation of a wetting PVP-film on the PDMS surface after polymerization of the IPN. Consequently, the reasoning for obtaining a transparent PVP/PDMS-IPN is similar as the arguments for obtaining a hydrophilic PVP/PDMS-IPN.

When dried, all of the PVP/PDMS-IPNs became opaque, irrespective of the solvent used during polymerization. Some samples were still transparent in the dry state but these samples contained less than 5% PVP in the PVP/PDMS-IPN. In the case of hexane used as polymerization media, there is no change in transparency before and after swelling in water (all samples were opaque).

An additional comment is that the transparency for some of the IPNs is varying at different locations. This indicates that PVP tend to cluster into denser regions in some parts of the PDMS matrix. The reason for this is not fully understood but one plausible explanation is local variations in crosslink density within the PDMS sheeting. The effect of varying transparency at different points of an IPN sample is seen through the variations of the error bars in Figure 2. Probably, the error bars could have been minimized by measuring the transparency in more than three points of the sample.

Characterization of phase domains in dry and wet PVP/PDMS-IPNs

This study shows that the transparency of the PVP/PDMS-IPN can be tuned by the choice of solvent and that the transparency of a PVP/PDMS-IPN polymerized in a solvent can be understood from the solubility parameter of the solvent. We have postulated that the domains have different size depending on the polymerization media. To measure the size of any such phase domains in the PVP/PDMS-IPN samples, X-ray scattering techniques on wet PVP/PDMS-IPN have been used. The SAXS measurements revealed no differences between

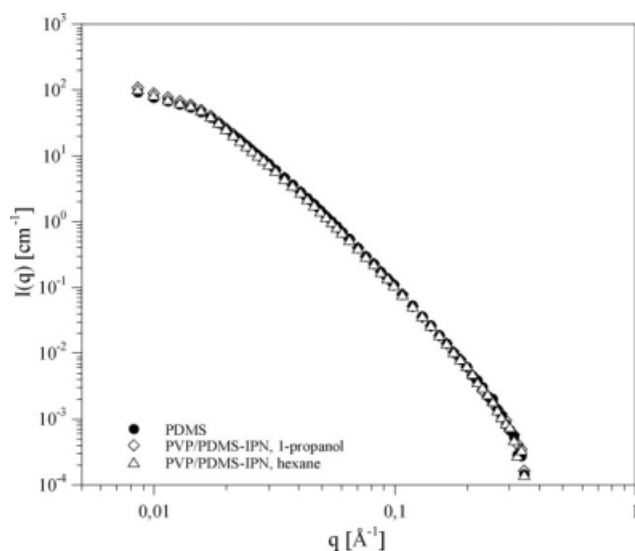


Figure 4 SAXS data for the PDMS sample and two different PVP/PDMS-IPN samples. One PVP/PDMS-IPN was polymerized in 1-propanol (19% PVP, 64% transparency) and the other PVP/PDMS-IPN was polymerized in hexane (29% PVP, 10% transparency).

PDMS and the PVP/PDMS-IPNs polymerized in 1-propanol or hexane (Fig. 4). All data show a so-called q^{-4} behavior, which shows that there are some structures with sharp interfaces, but since the curves overlap these interfaces and the correspond-

ing structures are very similar for the investigated samples. The data are very similar for all samples, including the PDMS reference, it is clear that the structures that give rise to the scattering are present already in the starting PDMS film, which is not swellable in water. Because the scattering has relatively high intensity, the structures have high contrast relative to the surrounding polymer matrix and this suggests that it originates from the silica filler, which we know is present in the PDMS film according to the supplier. The samples were also analyzed with XRD, where it is possible to determine the size of crystalline domains, but it was not possible to detect any such domains in the IPN.

Replicas of the PDMS sample and the PVP/PDMS-IPN exposed to water were analyzed with TEM. The TEM images in Figure 5 show that the PVP/PDMS-IPN has regions with a network structure, which does not appear in the PDMS. These regions, which are typically 250–350 nm in diameter, are suggested to belong to water-swollen regions, i.e., phase-separated PVP domains. For the TEM preparation, the water-swollen samples are extremely fast frozen, and then fractured prior to sublimation of the amorphous ice. During sublimation, the water molecules move from water-swollen PVP domains in the samples to the cold trap, thereby dehydrating the PVP domains which are still frozen in their swollen, expanded state. This

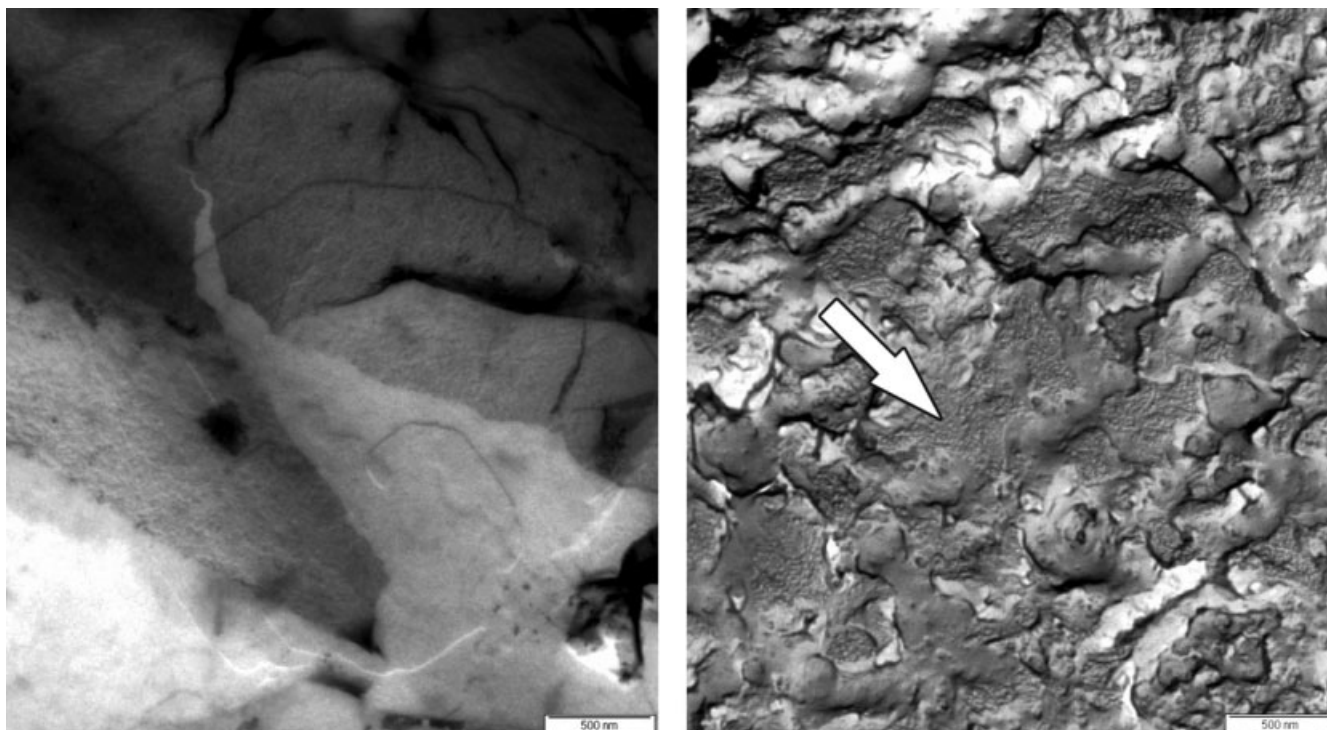


Figure 5 TEM images with magnification $\times 4646$ of (a) PDMS and (b) PVP/PDMS-IPN (polymerized in toluene, 27% PVP, 58% transparency). The arrow in the PVP/PDMS-IPN sample indicates a wrinkled area, which corresponds to a PVP-rich region.

process should generate a strong tension in the domains, which are forced to stay in the expanded state, despite the removal of the water which once caused the swelling. The replicas analyzed by TEM were generated at this point, and reflect this material, with its presumed tensions in the PVP domains.

For this reason, we believe that the wrinkled regions in Figure 5(b), marked with an arrow, should reflect the size and shape of the swollen PVP domains in the IPN material.

To further explore the phase domains in the material, dry samples were also analyzed by SEM. A few

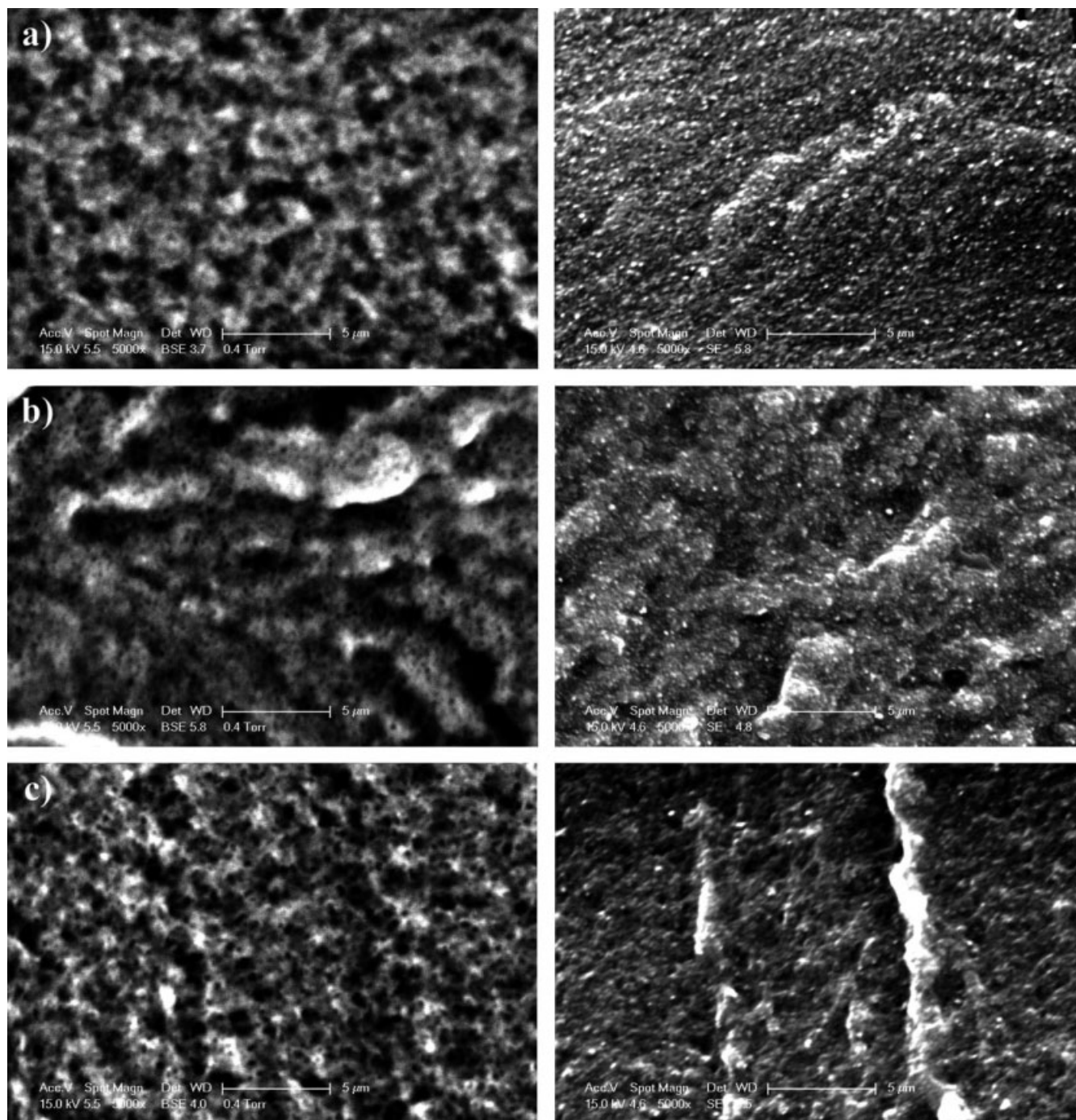


Figure 6 SEM images of (a) PDMS, (b) PVP/PDMS-IPN polymerized in 1-propanol (22% PVP, 82% transparency), and (c) PVP/PDMS-IPN polymerized in cyclohexane (20% PVP, 13% transparency). The left images are obtained with the BSE detector and the right image is obtained with the SE detector. The SE image is not exactly at the same position as the BSE image but the same morphology is seen throughout the whole sample. Note that the BSE images of the IPNs reveal the presence of PVP-rich regions (dark spots with a diameter 200–400 nm) in the IPN, which are not present in the SE images.

selected images are shown in Figure 6. The images were obtained with the BSE and SE detector. The reason for using different detectors is that they reveal different information about the sample. The BSE detector detects the contrast between areas of different chemical composition when the average atomic number in various regions is different. Brighter regions in the BSE image correspond to areas containing atoms of higher atomic number. On the other hand, in the SE image, topographical information in the sample is obtained.

The BSE image of PDMS [Fig. 6(a)] has dark and bright regions where the bright regions belong to silicon-rich areas, as it is the element in the material with the highest atomic number. Similar dark and bright regions are also visible in the BSE images of the two PVP/PDMS-IPNs [Fig. 6(b,c)], but in addition, smaller dark spots, giving the samples a sponge-like substructure, appear in the BSE images. This is especially prominent for the PVP/PDMS-IPN that was polymerized in cyclohexane [Fig. 6(c)] and has a low transparency, where many dark spots of larger diameter than the corresponding spots in the sample polymerized in 1-propanol [Fig. 6(b)] can be seen. Finally, we conclude that as the dark spots do not appear in the SE images, this confirms that they are indeed regions with different chemical composition than the original PDMS, and not areas of different topography.

The dark spots should belong to regions that are rich in carbon (the element with the lowest atomic number) or deficient in silicon, and the area that the dark spots cover in the SEM images for the two different IPN samples in Figure 6(b,c) are of the same order of magnitude. Presumably, not all of the PVP in the IPN sample is present as dark spots in the SEM images, there is also some part of the PVP concentration with smaller phase domains (approximately half of the total PVP concentration in the IPN sample) that cannot be detected in the SEM images. The size of the dark spots for the IPN with 13% transparency was 350 ± 16 nm, whereas the size of the phase domains was 180 ± 7 nm for the IPN with transparency 82%. This is also in good agreement with the phase domain sizes determined from the TEM analysis of a PVP/PDMS-IPN with similar PVP concentration but with 58% transparency. The size of the phase domains in this sample is in between those values obtained from the SEM images in Figure 6. According to the theories of light scattering, a sample will have lower transparency (i.e., more light is scattered) for larger particles. The size of the phase domains in all IPN samples are in the region for Mie scattering, and this theory suggests that the scattered light is proportional to the fourth power of the particle diameter.²² Our data is limited, but an attempt to fit the scattering of the IPNs to the meas-

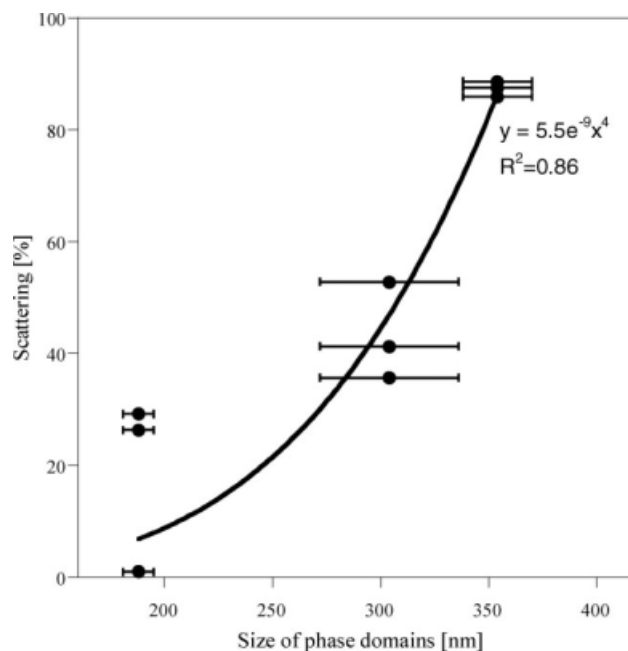


Figure 7 Curve fit to the Mie scattering theory for the measured phase domains in the PVP/PDMS-IPNs. The solid line represents a curve fit to the Mie scattering theory in which scattering is proportional to the fourth power of the size of the scattering objects.

ured phase domain sizes in Figure 7 showed an acceptable agreement with the Mie scattering theory. In Figure 7, the scattering was obtained through the following relation:

$$\text{Scattering} = 100\% - \text{Transparency of the IPN} \quad (4)$$

The phase domain values were the ones that were obtained from the SEM and TEM analysis as discussed earlier.

The glass transition temperature (T_g) is frequently measured to determine the degree of miscibility in the IPNs because the presence of two individual T_g s indicate phase separation in the IPN, whereas a shift in T_g s or one single T_g indicate compatibility on a molecular level between the polymers. PDMS has an extremely low T_g at -122°C (Fig. 8), which is in agreement with other literature references.^{18,19} On the other hand, PVP has a much higher T_g varying between 50 and 180°C , depending on the molecular weight and the water content in PVP.^{23,24} Unfortunately, PVP cannot be included as a reference material for the DSC measurements because it was not possible to synthesize a similar type of PVP as the one in the IPN. The molecular weight and the degree of crosslinking of the PVP in the IPN are unknown, and to have a PVP reference material these parameters need to be known.

In our case, it was not possible to detect the T_g for PVP in the IPN and the reason for this may be due to low molecular weight of PVP in the PVP/PDMS-

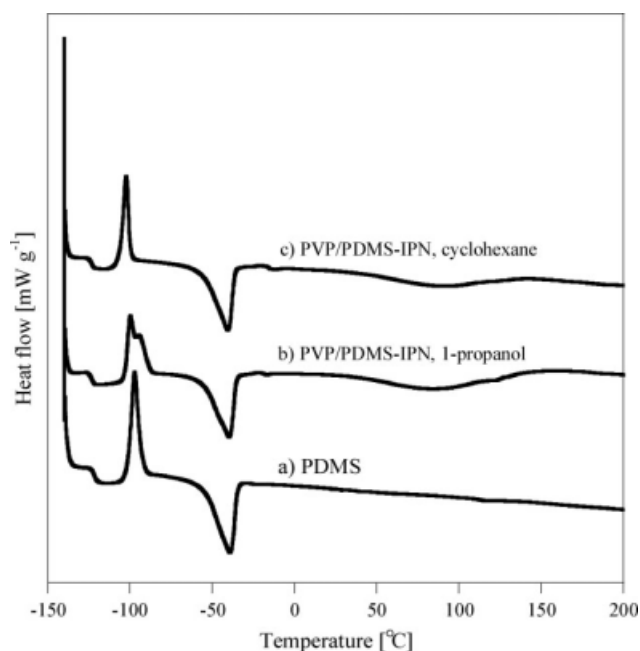


Figure 8 DSC data for (a) PDMS, (b) PVP/PDMS-IPN polymerized in 1-propanol (20% PVP, 79% transparency), and (c) PVP/PDMS-IPN polymerized in cyclohexane (20% PVP, 13% transparency). The T_g is at -122°C for all three samples.

IPN and the fact that the PVP concentration in the IPN was only 20%. However, the T_g for PDMS was clearly detected with DSC but the position and magnitude of the T_g in PDMS and in the IPNs were identical at approximately -122°C . Two other peaks were also present in the DSC curves and they represent cold crystallization of PDMS at -100°C and melting of the crystallites in PDMS at -40°C . In addition, for the IPN samples, a transition between 50 and 100°C was observed, which may be due to the effect of water in the PVP network. We conclude that the PVP/PDMS-IPN analyzed here was phase separated on a molecular level. Because the analyzed IPN samples were representative samples, we have reason to believe that all IPNs prepared in this study were fully phase separated on a molecular level, with phase domains below 350 nm.

CONCLUSIONS

Hydrophilic PVP/PDMS-IPNs with various concentrations of PVP in the IPN were prepared by using a two-step preparation method. The NVP concentration was varied as well as the organic solvent used during the synthesis. The following conclusions can be drawn from this study:

- The transition from a hydrophobic to a hydrophilic PVP/PDMS-IPN occurs at different PVP concentrations depending on the solvent. Gener-

ally, if the solvent has a similar solubility parameter as PVP, i.e., if it is a good solvent for PVP, a lower concentration of PVP in the PVP/PDMS-IPN is required to obtain a wettable surface.

- The solvent used during polymerization also has significant impact on the obtained transparency of the PVP/PDMS-IPN when it is swollen in water. This follows the same trend as the transition to a hydrophilic PVP/PDMS-IPN, i.e., a good solvent for PVP also results in higher transparency of the PVP/PDMS-IPN.
- The results are correlated with the solubility parameter of the solvent used during polymerization. It was found that di(ethylene glycol)ethyl ether is the most suitable solvent for acquiring both a transparent and hydrophilic PVP/PDMS-IPN.
- Phase domains, presumably consisting of phase-separated PVP in the PVP/PDMS-IPN, were detected and analyzed using several different techniques. It was found that the phase domains are approximately 350 nm when samples are polymerized in a nonsolvent for PVP, but smaller phase domains in the PVP/PDMS-IPN are found in samples which are polymerized in a good solvent for PVP, such as 1-propanol. This implies that a better mixing between PDMS and PVP is achieved for samples polymerized in a solvent with similar solubility parameter as PVP and that this gives smaller scattering units in the IPN, which, in turn, results in higher transparency.

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