

Synthetic hydrogels: 7. High EWC semi-interpenetrating polymer networks based on cellulose esters and N-containing hydrophilic monomers

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The formation of high (>70%) water content semi-interpenetrating polymer networks (IPNs) from combinations of cellulose esters and nitrogen containing hydrophilic vinyl monomers has been investigated. The properties of the resultant materials have been compared with those of copolymers of the same nitrogen containing monomers with a variety of methacrylate esters. Cellulose acetate and cellulose acetate butyrate were found to show acceptable solubility in the liquid monomers *N,N*-dimethyl acrylamide and *N*-vinyl pyrrolidone, which both possess adequate hydrophilicity, solvent power and polymerizability for IPN formation. In general the IPNs produced from the cellulose esters were observed to have higher equilibrium water contents than did the copolymers derived from the methacrylate monomers of similar hydrophilicity. Additionally, the detailed water binding properties of the two types of system showed considerable differences. Interpenetrating network formation produces materials that are stiffer and stronger but less elastic than the hydrogel copolymers of similar water content. In this behaviour these simple IPNs begin to mimic properties of biological hydrogel composites which differ from homogeneous synthetic hydrogels in the same way. The surface properties of the semi-interpenetrating materials are consistently different from those of the copolymers of comparable composition or equilibrium water content in that they have appreciably lower polar components (γ_p) of surface energy.

(Keywords: interpenetrating polymer networks (IPNs); water content; physical properties)

INTRODUCTION

Hydrogels occupy a unique position in the field of biomaterials because of the ways in which the imbibed water strongly influences the transport, surface and mechanical properties of the polymers. Some aspects of the effect of hydrogel structure and composition on the water binding¹, bulk, mechanical, surface^{2,3} and transport properties^{4,5} of the gels have been discussed in previous papers in this series. One recurring feature of such studies is the way in which increasing water content advantageously influences some aspects of behaviour (for example transport and interfacial properties) whilst disadvantageously reducing mechanical strength, thereby limiting the range of applications for these materials. In biological systems the existence of composite structures provides a method of combining good mechanical properties and a high water content⁶⁻⁸. Articular cartilage, based on an aqueous proteoglycan matrix with collagen as the filler polymer, is one example of such composites. This material has a high water content but excellent mechanical properties. There has been some attempt to reinforce hydrogel matrices with a second component to enhance their mechanical performance. However, there has been very little systematic work on hydrogel composites, particularly in the field of interpenetrating network and related polymer structures which may enable the design of synthetic hydrogels which mimic some aspects of the behaviour of biological composites. This work has been principally directed to the develop-

ment of improved wound dressing and implant materials and we have previously reviewed the use of hydrogel composites in these applications⁹.

In the past two decades much research has been carried out on polymer blends and composites, principally because of the enhanced mechanical properties which these materials often possess. However, there is still some confusion about the precise definition of blends and composites when applied to polymers. Although 'a mix of components which are inseparable and indistinguishable' has been defined as a blend while a composite has been defined as 'a material made of constituents which remain recognizable', problems arise when trying to use these terms on a molecular level. Mason and Sperling¹⁰, for example, have used the terms polyblend or polymer blend to refer to a system which contains two distinguishable types of polymer molecules. Their definition will be used throughout this work.

Interpenetrating polymer networks (IPNs) have been defined as a combination of two polymers, each in network form, at least one of which has been synthesized and/or crosslinked in the presence of the other¹¹. They have been used in a wide range of applications and several reviews have been published describing both these applications and the fundamental theory of IPNs¹²⁻¹⁶. In contrast, attempts to extend this technology to hydrogels have been few and unsystematic^{9,17-22}. They have been mainly concerned with the application of gradient IPNs to drug delivery devices¹⁸⁻²². IPN systems may be described as follows¹¹. Monomer I is polymerized

and crosslinked to give a polymer which is then swollen with monomer II plus its own crosslinker and initiator. Polymerization of monomer II *in situ* produces a sequential IPN. If only one polymer in the system is crosslinked the network formed is called a semi-IPN. With sequential polymerization four such semi-IPNs may be produced. If polymer I is crosslinked and polymer II is linear a semi-I-IPN is formed, while a semi-II-IPN is produced from a linear polymer I and a crosslinked polymer II. Inverting the order of polymerization produces the other two possible semi-IPN compositions. Simultaneous polymerization, of a solution of both monomers with their crosslinkers and initiators, by two different, non-interfering methods produces a simultaneous-IPN or SIN.

Although these materials are known as interpenetrating polymer networks, it is only if there is total mutual solubility that full intermolecular interpenetration occurs¹¹. In most IPNs there is, therefore, some phase separation but this may be reduced by chain entanglement between the polymers.

In this paper we describe initial investigations in the field of hydrogel composites and more particularly in the extension of the principles of IPN preparation to hydrogel systems. The aim of the work is to achieve some understanding of the behaviour of such systems and of the factors that influence and limit their formation. The ultimate objective is to enable the design of synthetic hydrogels which mimic some aspects of the behaviour of biological composites. The IPNs described in this paper are not true sequential IPNs but semi-II-IPNs. They are synthesized by dissolving the filler polymer in a solution of monomer and then crosslinking the monomer. These semi-II-IPNs will be referred to throughout this work as semi-IPNs.

EXPERIMENTAL

Monomers

Optical grade 2-hydroxyethyl methacrylate (HEMA) was supplied by Ubichem Ltd. with a certificate of analysis. *N*-vinyl pyrrolidone (VP; ex BDH), *N,N*-dimethyl acrylamide (NNDMA; ex Fluka), lauryl methacrylate (LMA; Aldrich) and methyl methacrylate (MMA; BDH) monomers were purified by reduced pressure distillation as described in the literature^{2,3}. Ethylene glycol dimethacrylate (BDH) and azo-bis-isobutyronitrile (Aldrich) were used as supplied as were cellulose acetate (BDH) and cellulose acetate butyrate (Polymer Consultants Ltd.).

Preparation of membranes

Xerogels were prepared using the previously described method by copolymerizing the monomers *in situ* between two glass plates separated by a gasket¹. For the synthesis of semi-IPN membranes, however, the filler polymer was dissolved in the monomer, ethylene glycol dimethacrylate 1.0% (w/w) and azo-bis-isobutyronitrile 0.5% (w/w). In order to speed up the dissolution process, especially in systems containing VP, the polymer was first dissolved in a carrier solvent (e.g. acetone, tetrahydrofuran, toluene) which was subsequently removed. Studies demonstrated that the solvent used to aid dissolution did not influence the measured properties of the final hydrated gel. The polymerization protocol described previously

was then followed, as was the subsequent hydration procedure for the polymerized membranes. In all cases the ratios of components of the polymerized systems are calculated on a weight to weight basis.

Equilibrium water content

The equilibrium water content (EWC) was calculated by weight difference as described in the first paper of this series¹. Small samples were cut from a hydrated sheet of the hydrogel and after the surface water had been removed, the samples were weighed then dehydrated overnight in a vacuum oven to constant weight. The EWC (100% × weight of water in the gel/total weight of hydrated gel) was calculated and the final value is an average of at least three determinations.

Differential scanning calorimetry

Thermograms were obtained using a Perkin Elmer differential scanning calorimeter, DSC2 fitted with a liquid nitrogen subambient accessory¹. This involves cooling small weighted samples (*c.* 2 mg) in sealed aluminium sample pans to 223 K to ensure the freezing of any supercooled water. A heating rate of 5 K/min produced well separated endothermic peaks in the region of the melting point of water. Using a calibration graph, produced from samples of pure water, the area under the endothermic peaks was converted to the weight of freezing water in the sample.

Surface properties

The surface energies of the hydrogels were probed using Hamilton's method, captive air bubble and conventional sessile drop techniques. The methodologies and nature of the results in each case have been fully described in previous papers^{2,3} but a brief resumé of the techniques will be presented here.

*Hamilton's method*²⁴. The samples were suspended in an optical cell, filled with distilled water saturated with *n*-octane. A small drop of *n*-octane was introduced onto the under surface of the sample and angular measurements were taken, for both the left and right contacting drop interfaces, (using either a travelling telescope or photographic technique²) and then averaged. This was repeated for at least three different octane droplets and the overall average value was taken. As both *n*-octane and water have the same dispersive component of their surface free energies, 21.8 mN/m, the dispersive component of the surface free energy of the sample cancels out which means that the polar component of the sample may be evaluated directly.

Captive air bubble technique. For this technique the sample is mounted as for the Hamilton method, but instead of an *n*-octane droplet, an air bubble of controlled volume is released from a microsyringe onto the sample surface. The air bubble was enlarged to a diameter of approximately 5–6 mm and then reduced to 2 mm and the needle retracted. Angular measurements were then taken in a similar manner to that described for the Hamilton method.

Sessile drop technique. The prepared sample was supported in a glass cell with optically perfect sides and a sessile drop of the wetting liquid was formed on the

surface of the polymer through a G 25 hypodermic needle. The contact angle was measured by taking a tangent to the drop surface at the three phase interface. At least six measurements were made on each polymer sample and each measurement was the average of the contact angles on either side of the sessile drop. Averaged values lay within a $\pm 2^\circ$ band. Standard samples of polymer surfaces were regularly used as internal checks on the reproducibility of the procedures.

This technique may be used in conjunction with the Owens and Wendt equation (equation 1)²⁵ to determine the surface free energies of polymers in the dehydrated state.

$$1 + \cos \theta = (2/\gamma_{lv})[\gamma_{lv}^d \gamma_s^d]^{0.5} + (\gamma_{lv}^p \gamma_s^p)^{0.5} \quad (1)$$

where θ is the contact angle of the wetting liquid with the solid, γ_{lv} the liquid-vapour interfacial free energy, γ_s the solid surface free energy and the superscripts p and d refer to the polar and dispersive fractions of the surface or interfacial free energy. Two wetting liquids which have been fully characterized for polar and dispersive components are used. By measuring the contact angles of the liquids on the polymer surface and solving the equations simultaneously, γ_s^p and γ_s^d , the polar and dispersive components of the surface free energy of the polymer may be determined.

Predictive methods. Direct measurement of surface free energy is often tedious and difficult. In these cases predictive techniques provide a useful basis for comparison. Two predictive techniques, based on molecular constitution, the parachor and cohesive energy density, were used in this work to predict surface energies and the predicted values were compared with experimental values. The theory behind these techniques has been discussed fully in part three of this series³.

Mechanical properties

The tensile properties of the hydrogels were investigated using a Testometric Micro 500 tensometer (with 100N load cell), interfaced with an Apple IIe computer and an Iiwatso SR6602 plotter. Samples of width 6.25 mm were cut from the hydrogel under test and these were held between the rubberized jaws of the tensometer. The tests were carried out using a crosshead speed of 10 mm/min and a gauge length of 10 mm. The tensile strength, elongation to break and Young's modulus of the sample under test were calculated. In addition, the program enabled stress/strain and load/elongation curves to be plotted and performed a statistical analysis of the five tests run on each sample. In general, the standard deviations ($\sigma_n - 1$) of the tensile strength and Young's modulus were less than 10%. For the elongations to break, however, the values of $\sigma_n - 1$ varied more widely (between 10% and 20%) with the IPNs showing more variability.

RESULTS AND DISCUSSION

Hydrogels with EWCs of 70% or higher have a special attraction, for example, for extended wear contact lenses, drug delivery systems and wound dressings. However, the high EWC has implications for the mechanical and surface properties of the hydrogels in addition to its advantageous effects on diffusional transport through the

gel. Vinyl pyrrolidone (VP) has been the main hydrophilic monomer used to obtain high water content hydrogels where stability to temperature, pH and tonicity is required². Although acrylamide is well known as a source of high EWC gels these are both physically unstable in environments where there are changes in pH or tonicity and hydrolytically unstable in long term use. For these reasons acrylamide is unsuitable for biomedical applications, especially as the monomer is a neurotoxin. In addition, acrylamide is a solid which cannot, therefore, be used for the type of semi-IPN formation described here. In contrast, the disubstituted *N,N*-dimethyl acrylamide (NNDMA) has several advantages for use in semi-IPN formation. It is a liquid with good solvent properties and has a structural resemblance to VP. Additionally, the presence of two methyl groups confers hydrolytic stability. Unfortunately, methyl groups lead to chain transfer, so the potential value of this monomer in high EWC hydrogels is limited by a low kinetic chain length, which manifests itself in imperfect and mechanically weak networks. In the context of the present work this monomer is ideal, as any improvement in mechanical properties resulting from semi-IPN formation is readily detectable and of great potential value. Modified cellulose present many advantages as the reinforcing polymer system. The interconnected ring structure of the polymer backbone, is quite different from that of vinyl polymers and can be obtained in a range of chemically modified forms. The esters, for example, offer appropriate solubility characteristics for semi-IPN formation with VP, NNDMA and monomers of similar structure, although solubility limitations mean that it is only possible to investigate partial molar ranges in all the IPN systems examined. As a baseline against which semi-IPNs based on partially esterified cellulose might be judged, the properties of copolymers of VP and NNDMA covering the EWC range of interest were first investigated. Methacrylate monomers containing ester functions ranging in nature from relatively hydrophilic (HEMA) to increasingly hydrophobic, through methyl methacrylate (MMA) to lauryl methacrylate (LMA), were chosen. These monomers were thus able to mimic some structural aspects of the partially esterified cellulose. *Table 1* summarizes the EWCs together with the percentage freezing and percentage non-freezing water (as determined by d.s.c.) for a range of VP and NNDMA copolymers. This information may then be used to calculate the water binding characteristics of the copolymers expressed in g water/g polymer.

The effect of incorporation of the hydrophilic comonomers VP and NNDMA on the water binding of HEMA copolymers is illustrated in *Figure 1*. The EWC and freezing water contents (listed in *Table 1*) rise, as expected, with progressive incorporation of the hydrophilic monomer, whereas the percentage of non-freezing water, in both the HEMA-VP and HEMA-NNDMA copolymers, appears to fall with incorporation of hydrophilic monomer. If the non-freezing water is expressed in terms of g water/g polymer (*Figure 1*), however, the expected trend, an increase in the relative quantity of non-freezing water with progressive hydrophilic monomer incorporation, is observed. Thus, the number of moles of non-freezing water/mol of polymer repeat unit increases from 2.8 for poly HEMA to 3.5 for the HEMA-NNDMA 60:40 copolymer and 3.4 for the HEMA-VP 60:40 copolymer. This reflects the progressive increase in the

Table 1 Equilibrium, freezing and non-freezing water contents for VP and NNDMA copolymers

Copolymer hydrogel composition	Equilibrium water content (wt%)	Freezing water content (wt%)	Non-freezing water content (wt%)
Poly HEMA	37.6	13.2	24.4
HEMA-VP 95:5	38.7	15.2	23.5
HEMA-VP 90:10	41.1	17.1	24.0
HEMA-VP 80:20	43.8	21.3	22.5
HEMA-VP 70:30	49.6	24.9	24.7
HEMA-VP 60:40	54.9	32.5	22.4
HEMA-VP 50:50	64.3	47.2	17.1
HEMA-NNDMA 95:5	41.3	15.1	26.2
HEMA-NNDMA 90:10	45.5	20.0	25.5
HEMA-NNDMA 80:20	53.6	31.6	22.0
HEMA-NNDMA 70:30	62.4	43.4	19.0
HEMA-NNDMA 60:40	70.5	54.6	15.9
NNDMA 1.0% x-linker	88.4	70.7	17.7
NNDMA 2.5% x-linker	80.1	55.9	24.2
NNDMA 5.0% x-linker	73.4	42.7	30.7
NNDMA 7.5% x-linker	69.1	35.0	34.1
NNDMA 10.0% x-linker	60.9	26.2	34.7
NNDMA-LMA 90:10	78.0	55.6	22.4
NNDMA-LMA 80:20	69.2	39.1	30.1
NNDMA-LMA 70:30	61.5	29.7	31.8
NNDMA-LMA 60:40	53.5	21.7	31.8
NNDMA-MMA 95:5	86.5	65.2	21.3
NNDMA-MMA 90:10	86.2	64.0	22.2
NNDMA-MMA 80:20	83.1	58.7	24.4
NNDMA-MMA 70:30	80.7	55.6	25.1
NNDMA-MMA 60:40	70.3	44.0	26.3
VP 1.0% x-linker	98.1	93.0	5.1
VP 2.5% x-linker	93.7	81.9	11.8
VP 5.0% x-linker	86.0	69.9	16.1
VP 7.5% x-linker	78.4	58.4	20.0
VP 10.0% x-linker	72.4	45.3	27.1
VP-LMA 90:10	80.0	57.8	22.2
VP-LMA 80:20	68.0	37.7	30.3
VP-LMA 70:30	58.4	26.4	32.0
VP-LMA 60:40	51.2	18.8	32.4
VP-MMA 90:10	82.3	53.4	28.9
VP-MMA 80:20	76.7	43.1	33.6
VP-MMA 70:30	67.8	31.3	36.5
VP-MMA 60:40	55.6	19.6	36.0
VP-MMA 50:50	38.6	3.5	35.1

proportion of more effective water binding sites in the polymer chain.

The compositions shown on these graphs are based on feed ratios. Whereas for the NNDMA copolymers described here the feed and matrix incorporated ratios will agree to within a few percent, for copolymers containing VP, there can be a large disparity between the feed ratio and copolymer composition². Therefore, direct comparisons of the relative hydrophilicities of NNDMA and VP cannot be made simply by comparing the water binding properties at the same feed compositions. This point will be evident from a subsequent comparison of the water binding results.

Copolymers of both VP and NNDMA with the hydrophobic monomers methyl methacrylate (MMA) and with lauryl methacrylate (LMA) have been examined (Table 1). The water binding results may be expressed in the same way (Figures 2 and 3) as those for the HEMA copolymers (Figure 1). The equilibrium, freezing and non-freezing water contents, with progressive incorporation

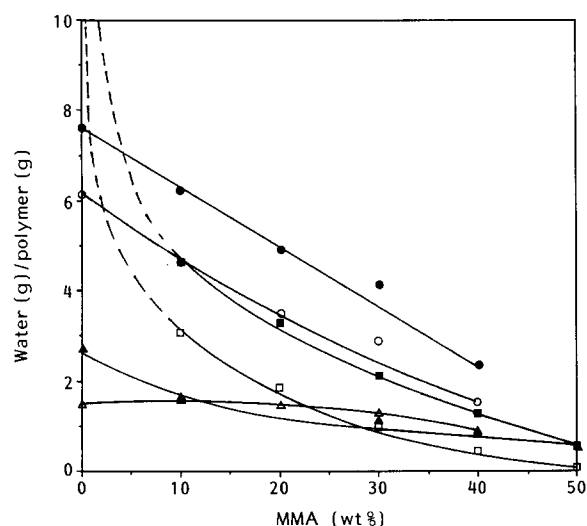


Figure 2 Effect of MMA incorporation on the water binding of VP-MMA (■, total water; □, freezing water; ▲, non-freezing water) and NNDMA-MMA (●, total water; ○, freezing water; △, non-freezing water) copolymers

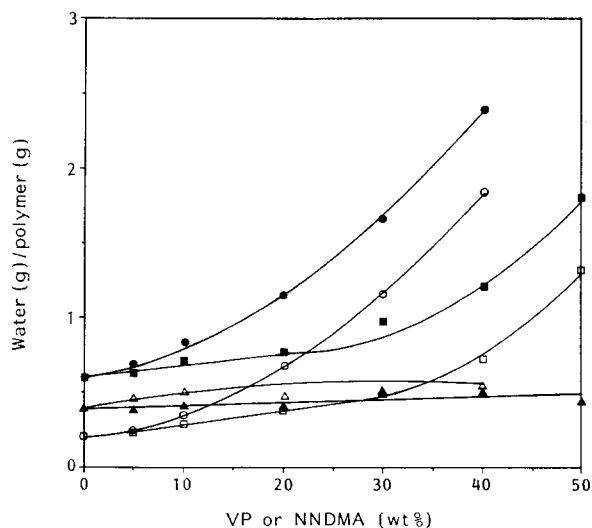


Figure 1 The water binding characteristics of HEMA-VP (■, total water; □, freezing water; ▲, non-freezing water) and HEMA-NNDMA (●, total water; ○, freezing water; △, non-freezing water) copolymers presented as a function of composition

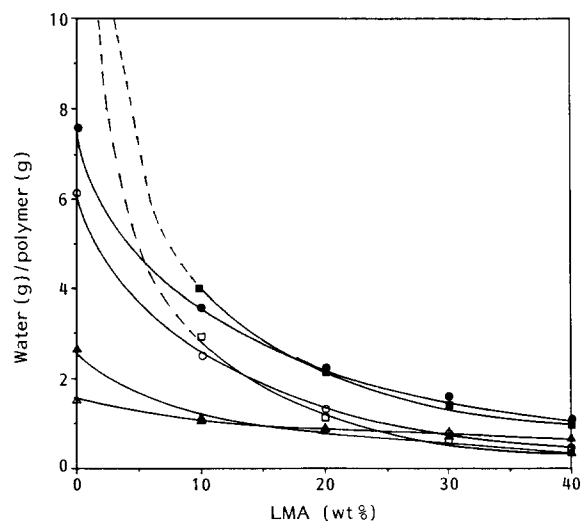


Figure 3 Effect of LMA incorporation on the water binding of VP-LMA (■, total water; □, freezing water; ▲, non-freezing water) and NNDMA-LMA (●, total water; ○, freezing water; △, non-freezing water) copolymers

Table 2 Mechanical properties of VP and NNDMA copolymer hydrogels (all the copolymers were clear and homogeneous)

Copolymer hydrogel composition	EWC (wt%)	Tensile strength (MPa)	Elongation to break (%)	Young's modulus	
				at 10% elongation (MPa)	at break (MPa)
Poly HEMA	37.6	0.50	198	0.51	0.25
HEMA-VP 95:5	38.7	0.48	194	0.57	0.25
HEMA-VP 90:10	41.1	0.53	174	0.74	0.30
HEMA-VP 80:20	43.8	0.32	74	0.76	0.43
HEMA-VP 70:30	49.6	0.35	76	0.75	0.46
HEMA-VP 60:40	54.9	0.25	117	0.51	0.21
HEMA-VP 50:50	64.3	0.20	97	0.43	0.20
HEMA-NNDMA 95:5	41.3	0.48	186	0.63	0.26
HEMA-NNDMA 90:10	45.5	0.39	131	0.70	0.30
HEMA-NNDMA 80:20	53.6	0.29	101	0.67	0.28
HEMA-NNDMA 70:30	62.4	0.25	116	0.52	0.21
HEMA-NNDMA 60:40	70.5	0.20	133	0.28	0.16
NNDMA 1.0% x-linker	88.4	0.14	141	0.10	0.10
NNDMA 2.5% x-linker	78.8	0.19	83	0.24	0.24
NNDMA 5.0% x-linker	73.4	0.23	47	0.54	0.54
NNDMA 7.5% x-linker	69.1	0.30	28	1.05	1.05
NNDMA 10.0% x-linker	60.9	0.24	22	1.32	1.11
NNDMA-LMA 90:10	78.0	0.21	105	0.23	0.20
NNDMA-LMA 80:20	69.2	0.42	217	0.28	0.19
NNDMA-LMA 70:30	63.7	0.43	174	0.63	0.25
NNDMA-LMA 60:40	53.5	0.53	317	0.85	0.17
NNDMA-MMA 95:5	86.5	0.13	149	0.12	0.09
NNDMA-MMA 90:10	86.2	0.16	170	0.15	0.10
NNDMA-MMA 80:20	83.1	0.13	130	0.18	0.10
VP-LMA 90:10	80.0	0.10	117	0.13	0.09
VP-LMA 80:20	68.0	0.30	115	0.46	0.26
VP-LMA 70:30	58.4	0.34	106	0.80	0.32
VP-LMA 60:40	51.2	0.44	117	0.89	0.38
VP-MMA 90:10	82.3	0.03	57	0.08	0.05
VP-MMA 80:20	76.6	0.13	110	0.19	0.12
VP-MMA 70:30	67.8	0.81	145	1.12	0.56
VP-MMA 60:40	55.6	2.65	157	12.32	1.69
VP-MMA 50:50	38.6	4.75	72	20.53	7.21

of hydrophobic monomer, follow the expected trend, although there are differences in the detailed water binding behaviour of NNDMA and VP. Thus, the incorporation of 20% MMA reduces the equilibrium water content of VP by 30% but that of NNDMA by only 7%. The more hydrophobic nature of lauryl methacrylate (in comparison to MMA) is reflected in its greater effect in reducing EWCs. The water binding behaviour of VP and NNDMA copolymers containing between 10% and 40% LMA is similar, expressed either as g water/g polymer (*Figure 3*) or in terms of EWC (*Table 1*). The more pronounced initial effect of hydrophobic monomers on VP is again apparent, with the incorporation of 10% LMA reducing the specific water binding expressed as g non-freezing water/g polymer by 60% for VP but by only 35% for NNDMA. The nature of the calculation involved in determining these quantities means that the error in this value increases with increasing water content. However, even after making allowances for this there is still a more significant apparent reduction of this value in VP copolymers than in NNDMA copolymers. This is in part a reflection in the difference in reactivity ratios of the relative comonomer pairs. Although appropriate experimental r_1, r_2 values are not available, for systems containing LMA, use of the Q-e scheme provides some illustration of the difference between the two systems. The calculated values are:

NNDMA:LMA, $r_1=0.54, r_2=0.74$, NVP:LMA, $r_1=0.061, r_2=0.78$. Experimental r_1, r_2 values are, however, available for the VP:MMA^{26,27} and NNDMA:MMA^{28,29} systems. Both the LMA and MMA copolymers show the same trend with NNDMA containing systems tending towards more ideal copolymerization behaviour.

VP and NNDMA copolymers: surface and mechanical properties

Tensile stress-strain curves were obtained for the range of hydrated copolymers described above and the derived parameters are collected in *Table 2*. The effect of EWC on the tensile properties of the hydrogel copolymers studied is compared in *Figure 4*. The general trend shown is a fall in tensile strength with increasing equilibrium water content. However, copolymer structure also has an important part to play in determining tensile strengths and it can be seen that the VP-MMA copolymers have much higher tensile strengths than would be expected from their EWCs. Thus, a 70-30 VP-MMA copolymer (with a water content of 68%) has a higher tensile strength than poly HEMA (having an EWC of 38%). Another interesting point associated with MMA incorporation (demonstrated in *Table 2*) is the sudden reduction in ϵ_b in the VP-MMA 50-50 copolymer. This illustrates the effect of reducing the freezing water content from 19.6% in the VP-MMA 60-40 copolymer to 3.5%

in this system. This correlation of freezing water content with the plasticizing role of water has been discussed in detail in an earlier part of this series³. It is quite clear that the behaviour of the VP-MMA copolymers is quite unusual in relation to the other hydrogels studied here. This point is most effectively discussed in the light of the results that will be presented for the semi-IPN hydrogels.

Semi-IPN hydrogels: water binding properties

A range of semi-IPN hydrogels based on the two nitrogen-containing hydrophilic monomers with cellulose acetate and cellulose acetate butyrate were prepared. The upper limits of cellulose acetate and cellulose acetate butyrate were defined in each case by the mutual compatibility and solubilities of the polymer/monomer systems. The water binding properties of the two semi-IPN systems were investigated in the manner described for the copolymers and the results are presented in Table 3. Some general observations may be made on

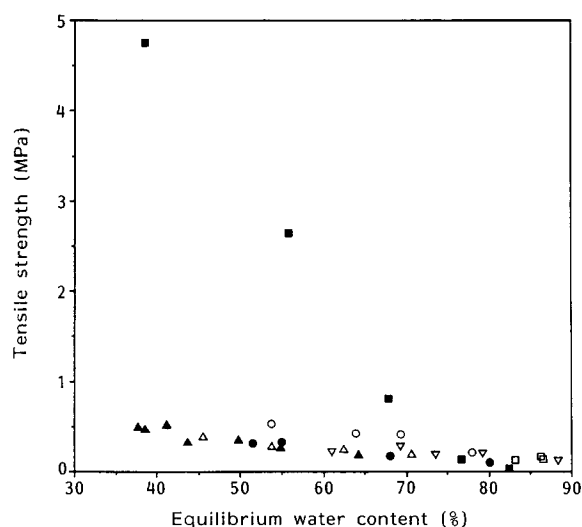


Figure 4 Tensile strengths of ▲, HEMA-VP; △, HEMA-NNDMA; ○, NNDMA-LMA; □, NNDMA-MMA; ●, VP-LMA and ■, VP-MMA copolymers presented as a function of equilibrium water content. The tensile strength of ▽, poly NNDMA with variation in water content is also shown

the relative effect of cellulose acetate and of cellulose acetate butyrate on the semi-IPNs formed with VP and with NNDMA. The more hydrophobic nature of cellulose acetate butyrate (in comparison to cellulose acetate) results, in all the systems, in a slightly greater drop in equilibrium water content. Significantly the difference lies in the freezing water content. This implies that the reduction in water content in the networks is a result of steric occlusion, in much the same way that hydrophobic styrene affects the water binding properties of hydrophilic monomers¹. It implies further that water binding to the substituted cellulosics is relatively ineffective and that they interact relatively little with the water binding sites in the hydrophilic monomers.

The comparative studies of both the copolymers and semi-IPNs based on VP and on NNDMA must be considered in the light of the difference in radical reactivity ratios of these monomers. Incorporation of VP in both types of system is relatively inefficient². This difference in the relative incorporation of VP and NNDMA offers at least a partial explanation of the fact that the progressive incorporation of methyl methacrylate, for example, appears to reduce the equilibrium water content of VP more effectively than that of NNDMA. Thus, the VP based copolymers and semi-IPNs appear to be deficient in VP and therefore, have lower EWCs and a lower water binding capability at a given (nominal) composition.

The effect of cellulose acetate and cellulose acetate butyrate incorporation into both *N*-vinyl pyrrolidone and *N,N*-dimethyl acrylamide gels lies between the relative effect of incorporating methyl methacrylate and lauryl methacrylate as comonomers. In this sense the copolymers produced with these methacrylates represent reasonable models for the semi-IPNs, the structures of the two types of system are quite dissimilar, however. It might be expected that the entanglement of the cellulosic chains with the hydrophilic polymer matrix would lead to an apparent increase in effective crosslinks in the matrix. The effect of the cellulosics is, however, quite different from the effect of covalent crosslinks of the type produced by ethylene glycol dimethacrylate incorporation. This is illustrated by comparing the effect of 10% incorporation of cellulose acetate and cellulose acetate

Table 3 Equilibrium, freezing and non-freezing water contents for IPNs of VP and NNDMA with cellulose acetate and cellulose acetate butyrate

IPN hydrogel composition	Equilibrium water content (wt%)	Freezing water content (wt%)	Non-freezing water content (wt%)	Appearance
NNDMA-CA 100:0	88.4	70.7	17.7	Clear
NNDMA-CA 98:2	84.7	64.8	19.9	Clear
NNDMA-CA 95:5	86.1	69.5	16.6	Clear
NNDMA-CA 90:10	82.1	64.5	17.6	Translucent
NNDMA-CA 85:15	79.8	59.1	20.7	Translucent
NNDMA-CAB 100:0	88.4	70.7	17.7	Clear
NNDMA-CAB 98:2	83.9	63.6	20.3	Clear
NNDMA-CAB 95:5	84.3	67.9	16.4	Translucent
NNDMA-CAB 90:10	80.0	61.0	19.0	Translucent
NNDMA-CAB 85:15	77.6	57.2	20.4	Translucent
VP-CA 100:0	98.1	93.0	5.1	Clear
VP-CA 90:10	87.2	77.2	10.0	Translucent
VP-CA 80:20	79.1	62.9	16.2	Translucent
VP-CAB 100:0	98.1	93.0	5.1	Clear
VP-CAB 90:10	81.8	69.8	12.0	Translucent
VP-CAB 80:20	72.6	57.8	14.8	Translucent

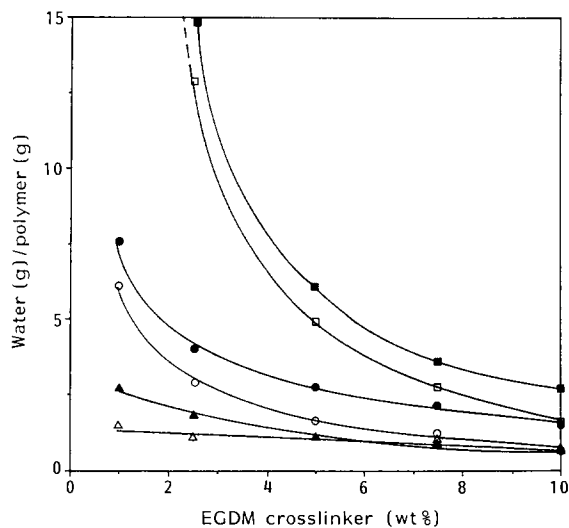


Figure 5 Effect of EGDM crosslinker incorporation on the \blacksquare , total water; \square , freezing water and \blacktriangle , non-freezing water in poly(vinyl pyrrolidone) and the \bullet , total water, \circ , freezing water and \triangle , non-freezing water in poly(*N,N*-dimethyl acrylamide)

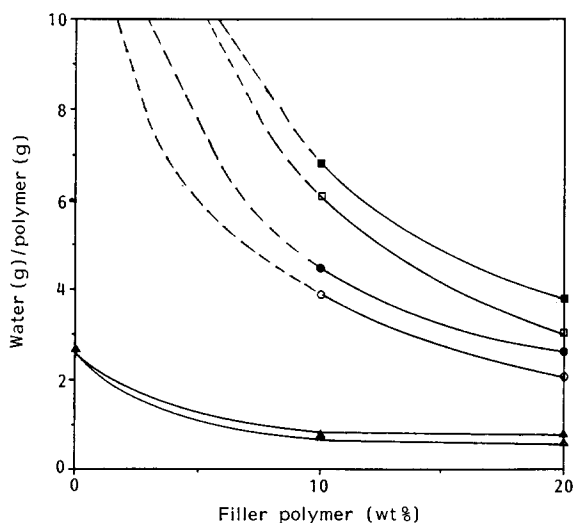


Figure 6 Effect of composition on the water binding of vinyl pyrrolidone-cellulose acetate (\blacksquare , total water; \square , freezing water and \blacktriangle , non-freezing water) and vinyl pyrrolidone-cellulose acetate butyrate (\bullet , total water; \circ , freezing water and \triangle , non-freezing water) semi-IPN hydrogels

butyrate (the similarity of which to incorporation of 10% methacrylate comonomer has been investigated) with the effect of 10% ethylene glycol dimethacrylate incorporation shown in Figures 5, 6 and 7. The retractive force of the relatively short crosslinks produced by ethylene glycol dimethacrylate incorporation clearly has little effect on the non-freezing water directly bound to the polymer backbone but decreases the freezing or bulk water much more effectively than does the incorporation of hydrophobic comonomer.

N,N-dimethyl acrylamide and *N*-vinyl pyrrolidone based semi-IPNs: mechanical properties

The mechanical properties of *N,N*-dimethyl acrylamide and *N*-vinyl pyrrolidone based semi-IPNs with cellulose acetate and with cellulose acetate butyrate are shown in Table 4. The values of tensile strength (σ_b), initial Young's modulus (E) and elongation to break (ϵ_b) for poly VP at low crosslink density are taken as zero

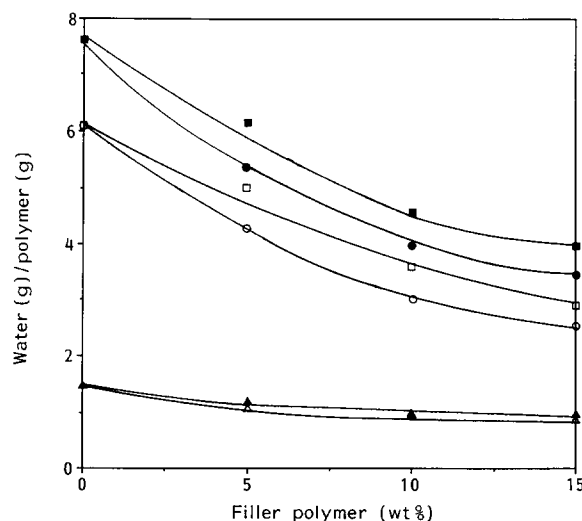


Figure 7 Effect of composition on the water binding of *N,N*-dimethyl acrylamide-cellulose acetate (\blacksquare , total water; \square , freezing water and \blacktriangle , non-freezing water) and *N,N*-dimethyl acrylamide-cellulose acetate butyrate (\bullet , total water; \circ , freezing water and \triangle , non-freezing water) semi-IPN hydrogels

Table 4 Mechanical properties of VP and NNDMA IPN hydrogels

IPN hydrogel composition	EWC (wt%)	Tensile strength (MPa)	Elongation to break (%)	Young's modulus	
				at 10% elongation (MPa)	at break (MPa)
NNDMA-CA 100:0	88.4	0.13	141	0.10	0.10
NNDMA-CA 98:2	84.7	0.12	97	0.19	0.12
NNDMA-CA 95:5	86.1	0.15	89	0.26	0.17
NNDMA-CA 90:10	82.1	0.18	58	0.83	0.31
NNDMA-CA 85:15	79.8	0.25	80	1.17	0.35
NNDMA-CAB 100:0	88.4	0.13	141	0.10	0.10
NNDMA-CAB 98:2	83.9	0.14	121	0.20	0.12
NNDMA-CAB 95:5	84.3	0.18	100	0.28	0.18
NNDMA-CAB 90:10	80.0	0.31	113	0.97	0.27
NNDMA-CAB 85:15	77.6	0.48	107	1.43	0.46
VP-CA 100:0	98.1	~0	~0	~0	~0
VP-CA 90:10	87.2	0.12	107	0.36	0.11
VP-CA 80:20	79.1	0.18	136	0.43	0.16
VP-CAB 100:0	98.1	~0	~0	~0	~0
VP-CAB 90:10	81.8	0.14	80	0.65	0.20
VP-CAB 80:20	72.6	0.38	79	1.58	0.59

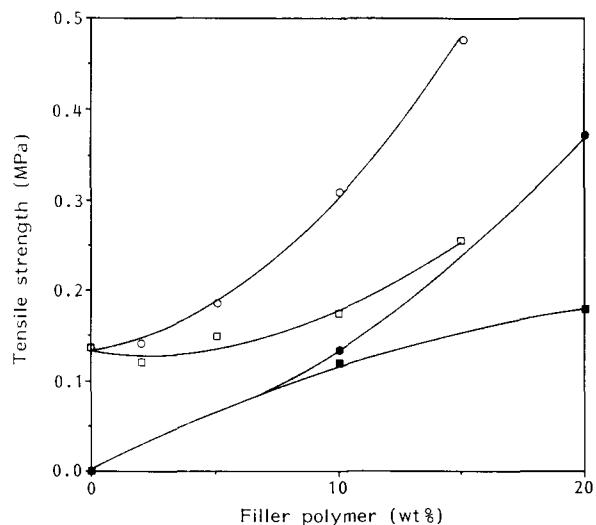


Figure 8 Variation in tensile strength with composition for ■, vinyl pyrrolidone-cellulose acetate; ●, vinyl pyrrolidone-cellulose acetate butyrate; □, *N,N*-dimethyl acrylamide-cellulose acetate and ○, *N,N*-dimethyl acrylamide-cellulose acetate butyrate semi-IPN hydrogels

because its mechanical properties are so poor that the pressure from the jaws of the tensometer frequently causes a fracture. If the tensile strength is examined as a function of composition several points emerge (Figure 8). The first is that semi-IPNs based on NNDMA have higher tensile strengths than the comparable VP based semi-IPNs. This demonstrates that the matrix polymer does have some influence on the tensile strength of these IPNs, which is clearly not determined solely by the tensile strength of the filler polymer. A second point illustrated in this figure is the increased tensile strength of IPNs in which cellulose acetate butyrate rather than cellulose acetate is the filler polymer. There are two possible explanations for the greater tensile strength of cellulose acetate butyrate containing IPNs. One is the structural difference between the two polymers. Although the lengthening of the pendent chains on the ring is a relatively minor structural change it may alter the configuration of the polymer in the matrix. A second possible explanation relates to the difference in hydrophobicity between cellulose acetate and cellulose acetate butyrate and is the lower water content of the cellulose acetate butyrate-containing IPNs. Against this point, however, is the fact that although the NNDMA-cellulose acetate 85:15 and NNDMA-cellulose acetate butyrate 90:10 IPNs have similar EWCs, the tensile strength of the cellulose acetate butyrate containing EWCs is approximately 20% greater. It appears that although the water content will have some effect on the tensile strength of these polymers, the structural differences between the polymers is the major controlling factor.

Incorporation of either cellulose acetate or cellulose acetate butyrate into hydrogels based on *N*-vinyl pyrrolidone and on *N,N*-dimethyl acrylamide generally leads to the formation of stronger and less flexible systems. The Young's moduli (E) of the materials show similar behaviour patterns to that of tensile strength, the values increasing with progressive incorporation of cellulose acetate or cellulose acetate butyrate into the IPN. Cellulose acetate butyrate once again has a more marked effect than cellulose acetate, leading to higher values of E in the cellulose acetate butyrate semi-IPNs than those

in which cellulose acetate is the filler polymer. Thus, both the stiffness and the strength of the system are increased by cellulose acetate or cellulose acetate butyrate incorporation. An interesting reflection of the extent to which the water content of the semi-IPN dictates the mechanical properties can be assessed from graphical presentations of either Young's modulus or tensile strength as a function of hydration. Figure 9 shows the variation of the Young's modulus at break of both the vinyl pyrrolidone and *N,N*-dimethyl acrylamide based systems with water content. The majority of results fall in a narrow band with E increasing as the EWC decreases reflecting the dual effect of filler polymer on Young's modulus and water content previously discussed. Some comparison has already been made of the relative water binding properties of copolymers and semi-IPNs. It is, furthermore, clear that the semi-IPNs based on VP and on NNDMA are stiffer and stronger than the copolymers of these monomers at equivalent water contents (Figure 10).

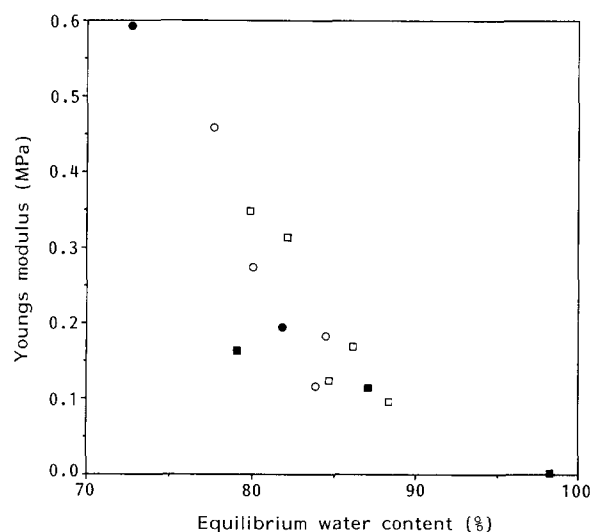


Figure 9 Variation in Young's modulus with equilibrium water content for ■, vinyl pyrrolidone-cellulose acetate; ●, vinyl pyrrolidone-cellulose acetate butyrate; □, *N,N*-dimethyl acrylamide-cellulose acetate and ○, *N,N*-dimethyl acrylamide-cellulose acetate butyrate semi-IPN hydrogels

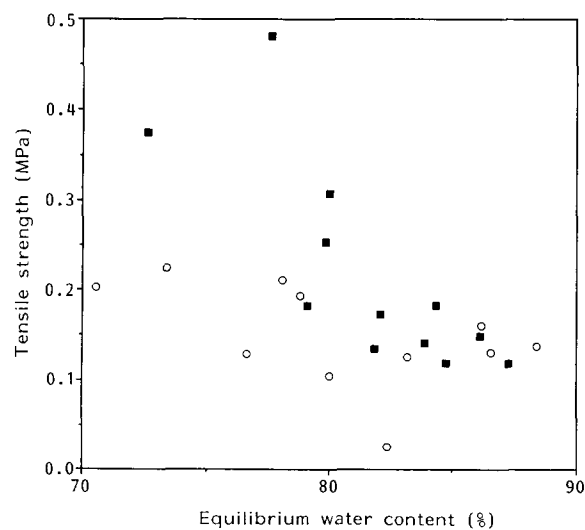


Figure 10 Effect of equilibrium content on tensile strength for a series of ○, copolymer and ■, semi-IPN hydrogels

Some preliminary comment must be made on the nature of the copolymers, in so far as they relate to those of the semi-IPNs. Although the vinyl pyrrolidone based systems are generally measurably weaker and less stiff than those based on *N,N*-dimethyl acrylamide at the same water content, the methyl methacrylate copolymers with these monomers depart from this pattern as the MMA level is increased. Thus, whereas the 50:50 HEMA-VP copolymer is less strong and less stiff than the 70:30 HEMA-NNDMA copolymer of similar water content, the 70:30 VP-MMA copolymer has a Young's modulus of more than twice, and a tensile strength of more than three times these levels, even though its water content is somewhat higher. Furthermore, this VP-MMA copolymer has superior mechanical properties to any of the NNDMA copolymers, even those at significantly lower EWCs. A similar situation exists with the 60:40 HEMA-VP copolymer, the 80:20 HEMA-NNDMA copolymer and the 60:40 VP-MMA copolymer. Surprisingly, vinyl pyrrolidone-lauryl methacrylate copolymers of similar water content do not have strength and stiffness values of the same order as the VP-MMA copolymers, rather they resemble those of the HEMA copolymers. The underlying reason for this behaviour lies in the differences in relative reactivity ratios of the vinyl pyrrolidone-methacrylate and the *N,N*-dimethyl acrylamide-methacrylate pairs. The disparity between vinyl pyrrolidone and the methacrylates leads to relatively long methacrylate blocks and the structure of copolymers begins to resemble those of semi-IPNs. The reason that methyl methacrylate blocks enhance mechanical properties more dramatically lies with the fact that the glass transition temperature of the segments is high ($> 100^{\circ}\text{C}$) and unaffected by the aqueous matrix. Whereas HEMA blocks have a similar glass transition in the dehydrated state this drops below room temperature in the hydrated state³. Although lauryl methacrylate is little affected by presence of water, the plasticizing effect of the long alkyl group again reduces the value of T_g to the region of room temperature. As a result the VP-MMA system is the only one in which the hydrogel is reinforced by segments of the appropriate strength and stiffness. The relevance of this model to semi-IPN systems will be explained in further papers. At this juncture it is sufficient to note the resemblance to semi-IPNs, in terms of the relationship of mechanical properties to EWC, of the VP-MMA copolymers. The unusually good mechanical properties of the VP-MMA system are well recognized, in the contact lens field, for example², although no previous attempt has been made to offer an explanation for this.

Two final observations relating to the mechanical properties of the semi-IPNs are worth making. The first is that the elongation to break is frequently adversely affected. The second is that in the cellulosic systems described here the networks are slightly heterogeneous and translucent. Addition of small amounts of both cellulose acetate and cellulose acetate butyrate does, however, produce clear, non-heterogeneous systems whose behaviour is slightly anomalous in comparison with that of the translucent heterogeneous members of the series. This applies to water binding behaviour in addition to mechanical properties.

Surface properties

We have previously described the assembly of tech-

niques that are used for the characterization of hydrogels in these laboratories^{2,3}. The polar and dispersive surface energy components (γ^p and γ^d) are first measured on the dehydrated material, these values being compared with those obtained by use of group contribution methods based on cohesive energy density and parachor. The results of these methods are presented for both copolymers and semi-IPNs in Table 5. The hydrated materials are then examined by inverted (captive) air bubble and octane (Hamilton) droplet technique which involve the study of samples immersed in water. These two measurements are used to generate the values of γ^p and γ^d for the hydrated material. The values are compared with those derived from the measured dehydrated values modified on the basis of a calculation involving the known water content of the gel (referred to as EWC-predicted)³. A further comparative value for the hydrated gel based on the entirely predictive parachor based technique is calculated. These various values for the hydrated materials are presented in Table 6.

Several points arise from the measured and predicted values of surface energies of the dehydrated materials. The previously observed phenomenon that measured polar components of surface energies of copolymers derived from two functional monomers are lower than those of the individual homopolymers² is also found in the results of Table 5. Thus, both HEMA-VP and HEMA-NNDMA copolymers show this effect, arising presumably from the acceptor-donor hydrogen bonding interaction of the two functional groups and the resultant increase in the surface contribution of the backbone hydrocarbon and α -methyl groups. In these, as in all copolymers, the higher polar components of the *N,N*-dimethyl acrylamide copolymers, relative to those of vinyl pyrrolidone, are evident. In copolymers both of *N,N*-dimethyl acrylamide and vinyl pyrrolidone with the alkyl methacrylates, the measured polar component falls steadily with increasing methacrylate concentration as would be expected. Predicted surface energy values obtained from CED-based and from parachor-based calculations show differences that relate to the underlying nature of these predictive techniques². The CED method reflects the dispersive component of surface energy and reasonable agreement with the measured dispersive components of the copolymers is found. Although the parachor based prediction should reflect the total surface free energy, relatively poor agreement is found especially in the case of the LMA containing copolymers. The method is limited by the difficulty in determining accurate density values, especially for poly(lauryl methacrylate), and by the inadequacy of group contribution data for complex monomers.

Although calculation methods require too many assumptions for them to be sensibly applied to the semi-IPNs, direct measurements of surface energy give reproducible and interesting results. The most significant general feature in comparing copolymers with semi-IPNs is that, in systems that have comparable water binding properties, the polar component of the surface free energy of the dehydrated semi-IPNs is noticeably lower than that of the corresponding (dehydrated) copolymers. The same general comment may be made about the measured values of hydrated surface energy (Table 6). Thus, the polar component of the semi-IPNs is generally lower than the measured polar component of the comparable copolymers and this effect is apparent in both the

Table 5 Measured and predicted surface free energies of dehydrated VP and NNDMA copolymer and semi-IPN hydrogels

Copolymer hydrogel composition	Parachor predicted surface energy (mN/m)	Measured surface energy			CED predicted surface energy (mN/m)
		γ^t (mN/m)	γ^p (mN/m)	γ^d (mN/m)	
Poly HEMA	50.5	50.5	20.2	31.4	39.1
HEMA-VP 95:5	50.4	46.5	9.5	37.0	39.1
HEMA-VP 90:10	50.4	45.5	6.2	39.3	39.2
HEMA-VP 80:20	50.4	44.3	4.6	39.7	39.2
HEMA-VP 70:30	50.4	43.4	3.4	40.0	39.3
HEMA-VP 60:40	50.4	43.3	3.3	40.0	39.3
HEMA-VP 50:50	50.5	43.9	4.1	39.8	39.4
HEMA-NNDMA 95:5	50.4	46.3	15.6	30.7	39.1
HEMA-NNDMA 90:10	50.4	45.6	13.9	31.7	39.0
HEMA-NNDMA 80:20	50.4	45.0	12.3	32.7	38.9
HEMA-NNDMA 70:30	50.4	44.1	10.2	33.9	38.8
HEMA-NNDMA 60:40	50.5	43.8	8.8	35.0	37.8
NNDMA 1.0% x-linker	52.6	50.7	18.7	32.0	38.0
NNDMA 2.5% x-linker	52.1	46.9	15.1	31.8	37.8
NNDMA 5.0% x-linker	51.4	45.0	14.4	30.6	37.4
NNDMA 7.5% x-linker	50.6	44.6	14.6	30.0	37.1
NNDMA 10.0% x-linker	49.8	43.2	13.8	29.4	36.8
NNDMA-LMA 90:10	55.6	49.0	15.6	33.4	37.6
NNDMA-LMA 80:20	56.9	47.1	12.8	34.3	37.0
NNDMA-LMA 70:30	57.3	46.7	11.4	35.3	36.5
NNDMA-LMA 60:40	57.0	46.6	10.6	36.0	36.0
NNDMA-MMA 90:10	52.0	47.0	12.0	35.0	37.9
NNDMA-MMA 80:20	51.1	46.5	9.8	36.7	37.7
VP 1.0% x-linker	51.1	46.1	12.6	33.5	39.7
VP-LMA 90:10	54.9	44.5	9.3	35.2	39.0
VP-LMA 80:20	57.2	44.5	8.5	36.0	38.3
VP-LMA 70:30	58.2	43.9	7.4	36.5	37.6
VP-LMA 60:40	58.2	44.3	7.3	37.0	36.9
VP-MMA 90:10	50.4	45.1	8.9	36.2	39.3
VP-MMA 80:20	49.7	45.2	8.2	37.0	39.0
VP-MMA 70:30	49.0	45.9	7.9	38.0	38.6
VP-MMA 60:40	48.3	45.6	7.4	38.2	38.2
VP-MMA 50:50	47.5	45.7	6.7	39.0	37.9
NNDMA-CA 100:0	52.9	50.7	18.7	32.0	38.1
NNDMA-CA 98:2	-	49.4	15.1	34.3	-
NNDMA-CA 95:5	-	47.0	12.0	35.0	-
NNDMA-CA 90:10	-	45.8	10.1	35.7	-
NNDMA-CA 85:15	-	44.8	9.1	35.7	-
NNDMA-CAB 100:0	52.9	50.7	18.7	32.0	38.1
NNDMA-CAB 98:2	-	52.1	16.2	35.9	-
NNDMA-CAB 95:5	-	48.1	10.5	37.6	-
NNDMA-CAB 90:10	-	47.4	9.3	38.1	-
NNDMA-CAB 85:15	-	46.8	8.9	37.9	-
VP-CA 100:0	51.1	46.1	12.6	39.7	39.7
VP-CA 90:10	-	43.2	5.9	37.3	-
VP-CA 80:20	-	42.4	5.1	37.3	-
VP-CAB 100:0	51.1	46.1	12.6	39.7	39.7
VP-CAB 90:10	-	45.0	7.0	38.0	-
VP-CAB 80:20	-	43.0	4.4	38.6	-

N,N-dimethyl acrylamide and vinyl pyrrolidone based semi-IPNs. A particularly significant illustration of this difference in behaviour is found in a comparison of the point at which γ^p and γ^d are approximately equal in copolymers and IPNs. In a previous paper³ it was shown that in simple hydroxyalkyl acrylate and methacrylate copolymer hydrogels this occurs at EWCs of around 10%. At higher EWCs the γ^p/γ^d ratio begins to approach that of water ($\gamma^p/\gamma^d=2.4$). In both the VP-CAB and NNDMA-CAB IPNs this equivalence of γ^p and γ^d occurs at water contents in excess of 70%. The equivalent copolymers, in contrast, have γ^p/γ^d ratios of 1.4–1.5 at these water contents.

With certain exceptions the use of measured values of dehydrated surface energies in conjunction with known water contents on hydration combine to give calculations of total surface free energies that agree well with measured values. One of the exceptions is the copolymer set based on HEMA and another functional monomer (NNDMA or VP). Here the low γ^t values of the dehydrated material coupled with the substantial volume fraction contribution that this makes to the hydrated gel (since the water contents are only moderate) produce predicted total surface energies that are well below measured values of γ^t . For a different reason the predicted water content values of γ^t for the semi-IPNs are very different from the

Table 6 Measured and predicted hydrated surface free energy of VP and NNDMA copolymer and IPN hydrogels

Copolymer hydrogel composition	Parachor predicted surface energy (mN/m)	Measured surface energy			EWC-predicted surface energy (mN/m)
		γ^t (mN/m)	γ^p (mN/m)	γ^d (mN/m)	
Poly HEMA	58.1	65.4	42.2	23.2	60.0
HEMA-VP 95:5	57.1	65.9	43.1	22.8	60.2
HEMA-VP 90:10	56.4	65.8	44.0	21.8	60.2
HEMA-VP 80:20	55.1	66.3	44.8	21.5	60.1
HEMA-VP 70:30	56.4	66.3	44.8	21.5	61.1
HEMA-VP 60:40	54.5	66.8	45.2	21.6	62.2
HEMA-VP 50:50	56.5	67.3	45.6	21.7	64.5
HEMA-NNDMA 95:5	57.7	66.3	40.8	25.5	58.6
HEMA-NNDMA 90:10	57.2	66.8	38.7	28.0	59.4
HEMA-NNDMA 80:20	56.6	66.5	37.7	28.8	59.5
HEMA-NNDMA 70:30	54.7	66.9	36.6	30.3	63.2
HEMA-NNDMA 60:40	55.4	67.1	36.1	31.0	65.1
NNDMA 1.0% x-linker	62.7	65.6	41.2	24.3	71.5
NNDMA 2.5% x-linker	—	65.1	40.2	24.9	68.3
NNDMA 5.0% x-linker	—	64.8	38.7	26.1	66.4
NNDMA 7.5% x-linker	—	65.7	36.1	29.6	65.2
NNDMA 10.0% x-linker	—	64.5	35.0	30.4	62.8
NNDMA-LMA 90:10	60.8	65.2	39.8	25.4	67.8
NNDMA-LMA 80:20	58.5	65.0	38.2	26.7	65.3
NNDMA-LMA 70:30	56.3	64.6	37.2	27.4	63.8
NNDMA-LMA 60:40	54.1	64.2	36.1	28.1	61.0
NNDMA-MMA 90:10	61.5	63.7	37.7	26.0	69.3
NNDMA-MMA 80:20	60.0	63.3	36.6	26.7	68.6
VP 1% x-linker	63.3	68.6	45.9	22.7	72.0
VP-LMA 90:10	61.0	66.0	42.2	23.8	67.6
VP-LMA 80:20	58.0	65.6	38.2	27.4	64.4
VP-LMA 70:30	55.0	63.7	37.7	26.0	61.5
VP-LMA 60:40	52.9	64.2	36.1	28.1	59.6
VP-MMA 90:10	61.0	65.7	40.8	24.9	68.3
VP-MMA 80:20	58.6	65.1	37.7	27.4	66.9
VP-MMA 70:30	55.5	64.8	36.6	28.2	64.9
VP-MMA 60:40	52.4	63.7	35.5	28.2	61.7
VP-MMA 50:50	47.6	63.3	34.4	28.9	57.2
NNDMA-CA 100:0	62.7	65.6	41.2	24.3	70.2
NNDMA-CA 98:2	—	65.3	37.2	28.1	69.3
NNDMA-CA 95:5	—	64.2	36.1	28.1	69.3
NNDMA-CA 90:10	—	63.8	35.0	28.8	68.1
NNDMA-CA 85:15	—	63.8	33.3	30.5	67.2
NNDMA-CAB 100:0	62.7	65.6	41.2	24.3	70.2
NNDMA-CAB 98:2	—	64.8	36.6	28.2	69.5
NNDMA-CAB 95:5	—	63.8	35.0	28.8	69.1
NNDMA-CAB 90:10	—	63.8	33.3	30.5	68.0
NNDMA-CAB 85:15	—	63.5	32.2	31.3	66.9
VP-CA 100:0	63.3	68.6	45.9	27.7	72.0
VP-CA 90:10	—	67.5	40.8	26.7	69.2
VP-CA 80:20	—	64.9	38.2	26.7	66.9
VP-CAB 100:0	63.3	68.6	45.9	22.7	72.0
VP-CAB 90:10	—	67.2	39.3	28.0	68.2
VP-CAB 80:20	—	65.2	32.2	33.0	65.4

measured values. Here the predicted values are very reasonable for this range of water contents and low measured values seem to reflect a genuine feature of semi-IPN behaviour, the surface adsorption of the more hydrophobic polymer. The polar component of surface energy of both hydrated, and to a lesser extent dehydrated materials, is thus consistently somewhat lower than that of comparable copolymers.

We have previously shown that direct measurements of hydrated surface energies by droplet techniques are distorted by the presence of an adsorbed water layer on the surface of the gel. Despite this, the chemistry of the matrix does contribute to the values determined by these

techniques and the equilibrium water content is not the sole determining factor in this respect. Thus, in examining a range of gels having different matrix chemistries we have shown that at a given equilibrium water content, a range of values of the polar component of the surface energy are obtained. This phenomenon is reflected in the results described here. The two monomers, vinyl pyrrolidone and *N,N*-dimethyl acrylamide, both possess hydrophilic water structuring groups that are relatively well shielded by non-polar hydrocarbon substituents. This in turn produces polar components of the surface free energy that lie towards the lower end of the spectrum of values obtained in gels of a given water content. As a result, this

whole group of materials (copolymers and semi-IPNs alike) are interesting in that they combine water contents in the region of 80% with polar surface energy components below 40 mN/m, the effect being more pronounced in the semi-IPNs.

CONCLUSIONS

The use of interpenetration techniques provides an interesting way of modifying the properties of hydrogels. The most obviously beneficial effects relate to mechanical behaviour, but water binding, surface and optical properties are also affected. The gross optical properties are related to compatibility phenomena, which occur at two levels. The initial solubility of filler polymer and matrix monomer governs the first essential step in semi-IPN formation. This process can be assisted by use of non-reactive solvents that are subsequently removed but this has no beneficial effect on the compatibility of matrix polymer and filler polymer in the dehydrated state. Compatibility considerations in the hydrated semi-IPNs are quite separate, involving as they do, water as the essential third component. All the semi-IPNs studied are clear (i.e. compatible) when dehydrated, when they are hydrated, however, differences in behaviour between the various compositions become apparent. At low levels (<5%) of filler incorporation all the hydrated semi-IPNs are clear. At higher concentrations of filler the semi-IPNs become translucent upon hydration to an extent that depends upon composition. Translucence in the hydrated systems is generally due to preferential water clustering around the more hydrophilic moieties to the exclusion of hydrophobic blocks.

Although initial interest centred on high water content, optically clear semi-IPNs for contact lens use, translucent or opaque materials are of potential value in such applications as wound dressings and synthetic articular cartilage. In this respect the marked effect that semi-IPN formation has in increasing initial modulus and tensile strength at the expense of elasticity is of considerable interest because these are the characteristic ways in which biological composite hydrogels differ from their homogeneous synthetic counterparts. The fact that unusual surface energy behaviour is observed in the IPN hydrogels is also of potential importance. The more detailed questions relating to the effect of the structure of the penetrant polymer on mechanical properties, compatibility and surface phenomena will be addressed in subsequent publications.

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