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Research paper

Macromolecule release and smoothness of semi-interpenetrating PVP–pHEMA networks for comfortable soft contact lenses

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Abstract

Knowledge about the microstructure and the release rate of hydrophilic macromolecules is required for a rational development of comfortable and safe contact lenses. Semi-interpenetrating networks of poly(hydroxyethyl methacrylate) (pHEMA) with poly(vinyl pyrrolidone) (PVP) were prepared by free radical polymerization of HEMA in the presence of PVP K30 or K90F, under anhydrous conditions or after addition of water, and evaluated in terms of swelling, porosity, PVP release rate, air–water surface tension, and friction coefficient. The greater water content was during polymerization, the higher was the swelling degree and porosity. Microphase separation above a certain volume of water resulted in hydrogels with bumpy surface and interconnected pores. All hydrogels showed a high optical clarity and slowly released PVP (20% after 9 days). In general, the greater the content of PVP or the higher its molecular weight was, the lower the friction coefficients were. In the case of hydrogels prepared with water, the friction was influenced by the balance between the ability to hold water in the network (which contributes to the sliding and PVP release) and the deleterious effect of an irregular surface. Controlled delivery of PVP revealed as a critical factor for improving the frictional behavior of pHEMA contact lenses.

Keywords: Semi-IPNs; Sustained release of poly(vinyl pyrrolidone); Comfortable lenses; Rheological evaluation of surface friction; Porosity

1. Introduction

Dry eye syndrome (DES) encompasses a heterogeneous group of ocular surface disorders that leads to an abnormal tear film and causes inadequate ocular lubrication [1]. When the homeostasis of the tear film is lost due to insufficient supply, excessive loss or anomalous composition of tears, the ability to protect the ocular surface epithelium decreases. As a consequence, DES also involves ocular surface epitheliopathy, tear hyperosmolality, unstable preocular tear film, and more or less intense inflammation and ocular irritation [2]. DES affects to 10–20% in adult population and up to the 70% of contact lenses wearers [1,3]. Except silicone lenses which do not absorb water [4], most contact lens alters the tear film increasing the evaporation and the discomfort at the end of the day, which causes 35% of wearers give up the use of contact lenses [5,6].

Although the prevention and management of DES requires a global approach [1], ophthalmic drops of hydrophilic polymers have been shown useful as tear film stabilizers, reducing the friction with the ocular tissues and washing out foreign bodies [7,8]. This prompted the incorporation of hydrophilic polymers to lens structure to be slowly released, wrapping the lens with a cushion-like layer able to soften the contact with the eye and the lid [9]. Polyvinyl alcohol (PVA) and poly(vinyl pyrrolidone) (PVP), which constitute two of the six categories of ophthalmic demulcents recognized by FDA [10], can be already found

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in some commercialized soft contact lenses [11,12]. Nelfilcon A lenses (i.e. functionalized PVA macromer) to which PVA was added during polymerization can sustain PVA release for several hours [13], showing an improvement in comfort related to enhancing wettability of the contact lenses [9]. PVP can be locked into etafilcon A (hydroxyethyl methacrylate-co-methacrylic acid) matrix and is claimed not to be released from the lens over one day of wearing; the increase in comfort being attributed to an enhancement in moisture retention and a reduction of the coefficient of friction [12], although no published data have been found.

For a rational understanding and design of lubricating lenses, a deeper knowledge of the effect of the hydrophilic polymer on their features is required. Despite the fact that contact lenses have been used for many years, their surface physical properties have received a little attention [14]. Linear polymers incorporated into cross-linked networks can act as dangling chains, resulting in a substantial reduction in the coefficient of friction [15], which could notably contribute to the comfort feeling. The time that the lens retains/controls the release of the hydrophilic polymer should be another key factor. The achievement of prolonged delivery not only for one day but also for one week, which is the time most disposable lenses are used, would have great practical interest. Compared to artificial tears that are intermittently applied, a sustained delivery from the soft contact lens could resemble better the lubrication role of natural tears.

The aim of this work was to design contact lenses based on poly(hydroxyethyl methacrylate), pHEMA, containing free chains of PVP forming semi-interpenetrating networks (semi-IPNs), and to elucidate the incidence of composition variables, such as molecular weight and proportion of PVP or volume of water added to the monomeric solution, on the PVP release rate and the frictional properties of the lenses. Addition of water to the monomers solution before polymerization may be motivated for different needs: (i) dissolution of high proportion of hydrophylic polymers; (ii) loading of colloidal particles to obtain drug sustained delivery [16]; and (iii) formation of a porous structure [17–19]. Since water is not a solvent for pHEMA, when its concentration is above the equilibrium water uptake of pHEMA, phase separation occurs during polymerization and the hydrogels become translucent or opaque. Therefore, an adequate control of water proportion in the monomer mixture is required to attain a wide range of porosities without altering the transparency of hydrogels [16]. In the particular case of soft contact lenses, porosity determines the degree of swelling and the mesh size of the network and, consequently, the diffusion of oxygen, nutrients and macromolecules through the hydrogel [19,20]. Since the porosity and hence a heterogeneous microstructure of the hydrogels can also affect PVP release rate and their sliding friction, these aspects were given special attention.

2. Materials and methods

2.1. Materials

Ophthalmic grade 2-hydroxyethyl methacrylate (HEMA) was from Merck (Darmstadt, Germany), and 2,2′-azobis(isobutyronitrile) (AIBN) and ethyleneglycol dimethacrylate (EGDMA) from Sigma–Aldrich (Madrid, Spain). Poly(vinyl pyrrolidone) (PVP) Kollidon® 30 of 44000–54000 Da and Kollidon® 90F of $1\ 10^6$–$1.5\ 10^6$ Da were from BASF (Barcelona, Spain). Purified water was obtained by reverse osmosis (MilliQ®, Millipore Iberica SA, Madrid, Spain). All other reagents were of analytical grade.

2.2. Hydrogels synthesis

The synthesis of the hydrogels was carried out in two different ways: at anhydrous conditions and in presence of different proportions of water. To prepare the anhydrous gels, EGDMA cross-linker (80 mM) and AIBN initiator (10 mM) were dissolved in HEMA (36 ml). The monomers solution was divided in 6 ml portions into which 0.3, 0.6 or 0.9 g of PVP K30 or 0.3 g of PVP K90F was added. Once dissolved, the monomers solutions were injected into a mould constituted by two glass plates covered internally with a polypropylene sheet and separated by a silicone frame 0.9 mm wide [21]. The moulds were then placed in an oven at 50 °C for 12 h and then heated at 70 °C for 24 h. Each gel sheet was boiled for 15 min to remove unreacted monomers and to facilitate the cutting of discs of 10 mm in diameter. Finally, they were dried in an oven at 50 °C. To check the reproducibility of the synthesis and the features of the hydrogels, the hydrogel with 0.9 g of K30 was synthesized and evaluated twice. Another set of hydrogels was prepared as follows: EGDMA (80 mM), AA (100 mM) and AIBN (10 mM) were dissolved in HEMA (30 ml). Mixtures of these monomers and water at volume ratios of 5.4:0.6, 4.8:1.2, 4.2:1.8, 3.6:2.4, 3:3, and 2.4:3.6 were prepared. To 6 ml portions of these solutions 0.9 g of PVP K30 was added. Once dissolved, they were injected into the moulds, polymerized and washed as described above.

2.3. Hydrogels characterization

2.3.1. Elemental analysis

The content in nitrogen of each hydrogel was determined using a Carlo-Erba 1108 Elemental Analyzer (Fisons Instruments, Ipswich, UK).

2.3.2. FTIR analysis

IR spectra of the hydrogels were recorded over the range 400–4000 cm^{-1}, in a Bruker IFS 66V FT-IR (Ettlingen, Germany) spectrometer using the KBr pellet technique.

2.3.3. Swelling kinetics

Dried hydrogels were weighed (W_0) and placed in 15 ml of water at 25 °C. Swelling, Q_t at various times t was calculated as relative weight gain; the sample being weighed (W_t) on each occasion after careful wiping of its surface with a soft tissue:

$$Q_t = 100(W_t - W_0)/W_0 \quad (1)$$

2.3.4. Porosity

Porosity, ε, of the hydrogels was determined from the equilibrium water content according to the model of Yanagawa et al. [19], which takes into account the water molecules present in the non-porous phase:

$$\varepsilon = (W_W - W_0 - W_{\mathrm{wnp}})/W_{\mathrm{w}} \quad (2)$$

where W_{w} is the weight of the swollen porous hydrogel, W_0 is the weight of the dry porous hydrogel, and W_{wnp} is the amount of water in the non-porous phase. The value of W_{wnp} of each hydrogel was estimated as:

$$W_{\mathrm{wnp}} = (W_{\mathrm{wnh}} - W_{\mathrm{dnh}}) \cdot W_0/W_{\mathrm{dnh}} \quad (3)$$

where W_{wnh} and W_{dnh} are the weights of swollen and dry non-porous hydrogel, respectively.

2.3.5. Transmittance

The transmittance of swollen discs immersed in water was recorded between 190 and 800 nm using an Agilent 8453 (Böblingen, Germany) spectrophotometer.

2.3.6. Scanning electron microscopy (SEM)

Water-swollen discs were immersed in liquid nitrogen, cut and stored at −80 °C for one day before freeze-drying. The samples were mounted on double-sided tape on aluminum stubs and sputter-coated with gold/palladium. Micrographs of the surface and the transversal cut were taken using a LEO-435VP (Leo Electron Microscopy, Cambridge, UK) apparatus.

2.3.7. PVP release test

Hydrogel dried discs were immersed in 20 ml water, 10 ml samples were taken every 24 h and this volume was replaced with fresh water. Each sample was mixed with 5 ml of 0.2 M citric acid solution and 2 ml of I_2/KI (0.81 g of freshly sublimed iodine and 1.44 g of KI in 1000 ml of water). After exactly 10 min, the absorbance of the solution was measured at 420 nm (Agilent 8453, Böblingen, Germany) against a blank prepared with water instead of the PVP solution [22]. The experiments were carried out in quadruplicate.

2.3.8. Friction force

The friction force of water-swollen discs was measured, in duplicate, at 25 °C using a Rheolyst AR1000N rheometer (TA Instruments, Crawley, UK) equipped with an AR2500 data analyzer and a Peltier plate. The discs were immersed in 11 ml of water and analyzed, in duplicate, after 1, 2, 3 and 4 days. The surface of the discs (11.9 mm diameter) was blotted with filter paper and immediately glued (Loctite® Super Glue-3, Henkel, Barcelona, Spain) to a 4 cm steel plate geometry. One milliliter of the aqueous medium was put on the surface of the Peltier plate and the geometry was moved towards the plate to an initial gap of 1 mm. The experiment consisted of a conditioning step applying 5 ± 0.1 N normal force (W) for 15 min and a peak hold step with an angular velocity of 0.05 rad/s for other 15 min. Since the velocity changes with the distance from the center of the axis, the obtained torque, T, is a total value over the velocity range from 0 to ωR, where R is the radius of the gel disc. The total friction, F, and the coefficient of friction, μ, were determined as follows [23]:

$$F = \frac{4T}{3R} \quad (4)$$

$$\mu = \frac{F}{W} \quad (5)$$

At each sampling time, the amount of PVP released was determined (as described above) in the medium from which the analyzed discs were taken.

2.4. Characterization of PVP solutions

2.4.1. Surface tension

The surface tension of PVP solutions in water (10–60 mg/l) was measured, in triplicate, by the platinum ring method using a Lauda Tensiometer TD1 (Königshofen, Germany) applying the needed density corrections.

2.4.2. Bound water

PVP solutions (5–30%) were stored at room temperature for 72 h and then sealed in aluminum pans and placed in a differential scanning calorimeter DSC Q100 (TA Instruments, New Castle DE, USA) with a refrigerated cooling accessory. The samples were cooled to –30 °C and heated to 60 °C, at 5 °C/min, to determine the amounts of free water and freezing (interfacial) water. The experiments were carried out, in triplicate, using nitrogen as purge gas at a flow rate of 50 mL/min. The calorimeter was calibrated for baseline using no pans, for cell constant and for temperature using indium (melting point 156.61 °C, enthalpy of fusion 28.71 J/g), and for heat capacity using sapphire standards. The enthalpy of the melting/freezing peaks was referred to the amount of water in each sample. The melting enthalpy of pure water (0% PVP) was 340 J/g. A plot of the melting enthalpy vs. PVP concentration (% w/w) gave a straight line. The PVP concentration that corresponded to the zero enthalpy indicated the composition of the PVP solution in which all water is bounded to the polymer.

3. Results and discussion

3.1. Swelling and microstructure of the hydrogels

PVP K30 was easily dispersed in HEMA up to 0.15 g/ml. By contrast, the greater molecular weight and

thickening ability of PVP K90F prevented a homogeneous mixing in proportions above 0.05 g/ml, and thus only this concentration of K90F was assayed. Once all components were added to the monomers solutions, the polymerization was carried out immediately to prevent crystallization or precipitation of any component, particularly AIBN, when water was added to the reaction mixture [18]. Hydrogels synthesized in the absence of water were completely transparent and showed a continuous and homogeneous surface. By contrast, those hydrogels made with monomer:water proportions of 4.2:1.8 visually evidenced some points of microphase separation, which rose in number and dimensions as the proportion in water increased. It was previously observed that pHEMA hydrogels do not phase separate when the content in water is below the saturation value of the gel (swelling equilibrium). By contrast, above this value, the exceeded amount of water phase separates and disperses in micron-sized regions of the network creating pores after polymerization [24]. Once synthesized, the hydrogels were boiled, which is a common method of cleaning and sterilizing contact lenses.

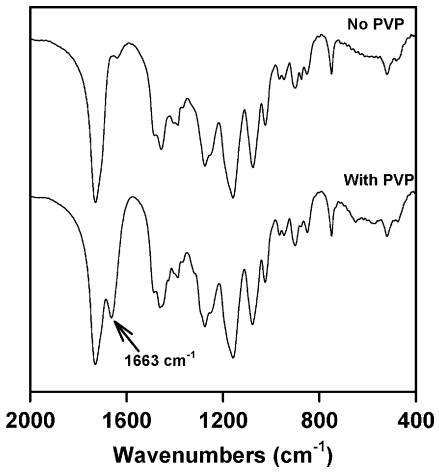

Fig. 1. FTIR spectra of pHEMA hydrogels prepared without PVP or with 128.6 mg PVP per gram of dried hydrogel.

All hydrogels featured the bands characteristic of pHEMA; mainly the C=O ester groups at 1727 cm^{-1}. The absorbance at 1663 cm^{-1} due to the C=O and N–C stretching vibrations of PVP increased as its content in the hydrogels raised [25]. The peak of unreacted C=C bonds at 1637 cm^{-1} was not observed (Fig. 1). To determine the amount of PVP remaining in the hydrogels after

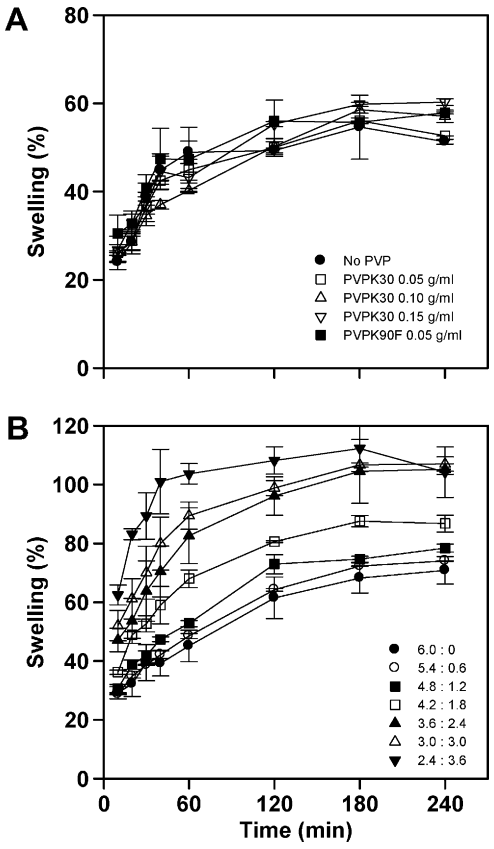

Fig. 2. Swelling profiles of (A) pHEMA hydrogels synthesized incorporating different proportions of PVP K30 or K90F, in the absence of water; and (B) pHEMA hydrogels prepared with 0.15 g of PVP K30 per ml and different monomer:water v/v ratios.

Table 1
Proportions of the main components used to synthesize the hydrogels, expected contents in PVP K30 and nitrogen, observed nitrogen content, porosity and PVP K30 release rate (fitting to square-root kinetics provided in all cases $R^2 > 0.95$)

Composition of the synthesis mixture HEMA:water:PVP	Expected PVP content (mg/g monomers plus PVP)	Expected *N* (%)	Observed *N* (%)	Porosity	Release rate ($day^{-0.5}$)
6.0:0:0	0	0	0	–	–
6.0:0:0.3	46.9	0.56–0.59	0.41	–	0.038
6.0:0:0.3[a]	46.9	0.56–0.59	0.59	–	0.039
6.0:0:0.6	89.5	1.07–1.15	1.12	–	0.030
6.0:0:0.9	128.6	1.54–1.64	1.49	–	0.027
5.4:0.6:0.9	142.8	1.71–1.83	1.39	0.020 (0.006)	0.033
4.8:1.2:0.9	157.9	1.89–2.02	1.69	0.018 (0.004)	0.026
4.2:1.8:0.9	176.5	2.12–2.26	1.67	0.077 (0.012)	0.048
3.6: 2.4: 0.9	200.0	2.40–2.56	2.03	0.132 (0.029)	0.066
3.0:3.0:0.9	230.7	2.77–2.95	2.29	0.145 (0.019)	0.059
2.4:3.6:0.9	272.7	3.27–3.49	2.72	0.150 (0.025)	0.079

[a] PVP K90F was used instead of K30.

boiling, the proportion of N (which is only present in PVP at 12–12.8%) was quantified by elemental analysis and compared with the predicted contents assuming that no PVP was lost during boiling (Table 1). In the set of hydrogels prepared in absence of water, only the one containing the lowest proportion of K30 showed a small lost of PVP. On the other hand, as the proportion of water in the polymerization medium increased, the more significant the amount of PVP washed out during boiling. Nevertheless, most PVP still remained in the hydrogels.

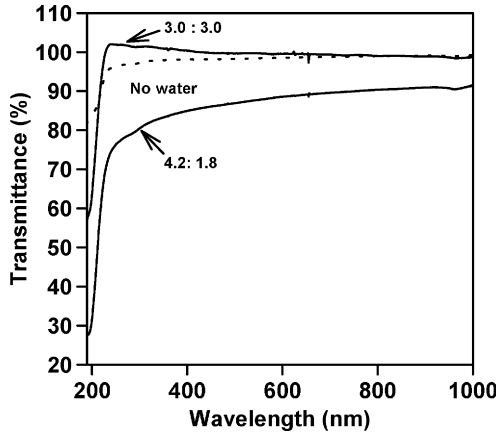

Fig. 3. UV–vis transmittance of some PVP–pHEMA hydrogels prepared with different monomer:water v/v ratios.

The different losses of PVP during boiling can be related to the important differences observed in the degree of swelling and porosity of the hydrogels. Those prepared at anhydrous conditions did not show influence by PVP, either on the swelling rate or the equilibrium swelling degree (Fig. 2A). By contrast, the porous hydrogels prepared in the presence of water remarkably increased their swelling as the proportion of water used in the synthesis rose (Fig. 2B). Porosity values obtained from the comparison of the aqueous swelling of each hydrogel synthesized in presence of water with that of the hydrogel of the same composition prepared in absence of water are shown in Table 1. This approach has been developed to estimate the increase in porosity caused by the synthesis in the presence of water, assuming that the ability to bind water by the polymeric chains after hydrogel synthesis is the same disregarding the content in water during polymerization [19]. This hypothesis is plausible since the composition of the hydrogels is the same and their cross-linking degree is quite low and, consequently, the mobility of the chains should not be impeded by entropic constrains. Replacement with water of 0.6 or 1.2 ml of monomer solution (from a total volume of 6 ml) only led to a minor increase in swelling and porosity. Volumes of 1.8 to 3.6 ml of water

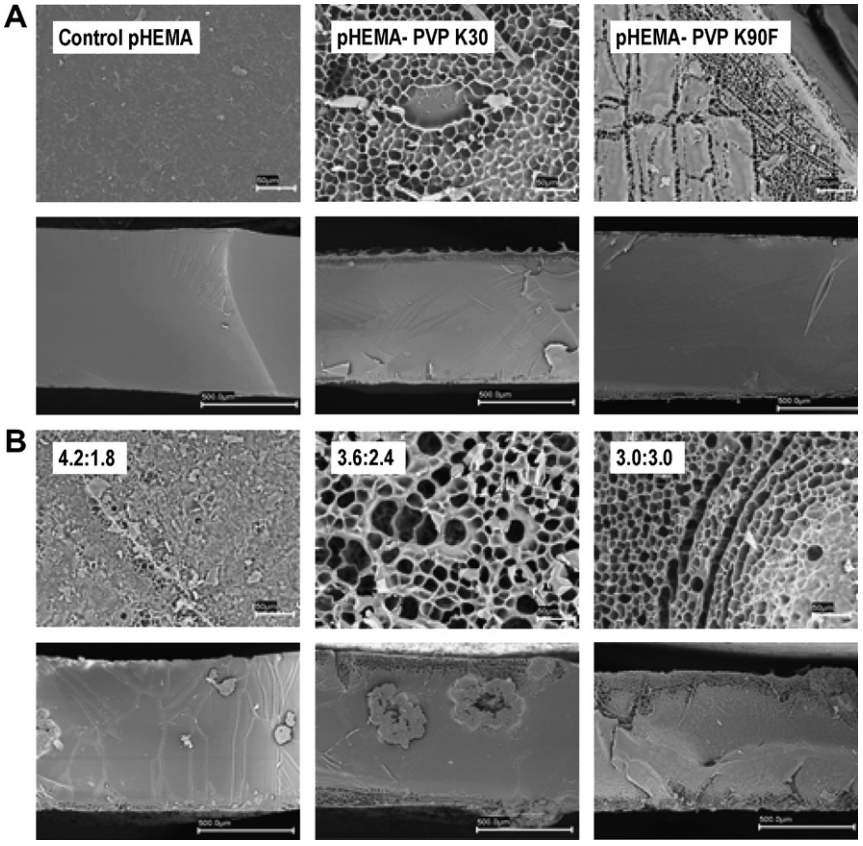

Fig. 4. SEM photographs of the surface (top) and the transversal section (bottom) of (A) pHEMA hydrogels synthesized without or with PVP K30 or K90F, in the absence of water; and (B) pHEMA hydrogels prepared with 0.15 g of PVP K30 per ml and different monomer:water v/v ratios.

progressively increased the porosity of the hydrogels up to a 15%.

The transmittance at 600 nm is commonly used as an index of the transparency of the contact lenses. All hydrogels at the swollen state gave values above 85% transmittance; most of them being above 95%. The maximum transparency in the whole visible range corresponded to non-porous pHEMA-hydrogels and to the porous hydrogels with high swelling degree (Fig. 3). pHEMA hydrogel used as control (i.e. prepared without PVP or water) just showed a minor decrease in transmittance below 200 nm. The transmittance of the hydrogels is conditioned by the light absorption (PVP absorbs below 200 nm) and on the light scattering. The light scattering of porous hydrogels not only depends on the size and distribution of pores, but also on their content in water; these factors contributing in an opposite way [20,24]. In the case of hydrogels synthesized in presence of water, the minimum in transmittance was observed for those prepared with 4.2:1.8 monomer:water proportion; hydrogels made with lower content in water (low porosity) or greater content in water (more swollen) being more transparent. Nevertheless, all PVP–pHEMA hydrogels can be considered to have an excellent optical clarity.

SEM images of freeze-dried hydrogels provided additional information on porosity and evidenced differences in surface morphology among the swollen hydrogels (Fig. 4). Freeze-drying of the specimens usually yield good images of the polymer matrix as it is in the swollen state, if no melting of the solvent occurs during the drying [26]. This was the case in our experiments. The control pHEMA hydrogels prepared without PVP had the smoothest surface and no pores were observed. The only minor irregularities found may be due to some swollen non-crosslinked pHEMA chains anchored to the pHEMA network, which could contribute to the low adhesive force of contact lenses as reported by Kim et al. [27]. The greater the content in PVP, the more uneven the surface of the freeze-dried hydrogels was. This could be due to the PVP which was being released from the lens. The transversal cuts indicated that the lenses have a homogeneous inner structure without apparent pores and that the chains of PVP which are still partially attached to the network may form polymer brushes at the lens surface. On the other hand, we observed that hydrogels synthesized in aqueous medium showed a spongy-like structure with a quite bumpy surface in the case of those prepared with 1.8 ml or more water (in a total of 6 ml). These latter hydrogels presented protuberances of polymer network and craters that came from inner parts of the hydrogel, which showed interconnected pores. These observations are mainly related to the microphase separation during synthesis, which leads to domains of different densities in the polymer.

3.2. PVP release

Fig. 5 shows the amounts of PVP released from the hydrogels prepared without water. These hydrogels showed a fast delivery of PVP in the first 24 h and then the release became more sustained. Similar behavior was observed for hydrogels prepared with water. Despite the important amount of PVP released, the relatively high initial load of the lenses and their sustained delivery made it possible for the content of the discs in the PVP to be still high on the 9th day of the assay (ca. 80% of the initial PVP amount). The release profiles were well fitted to square-root kinetics (Table 1), which means that diffusion is the main mechanism involved in the release, as expected for

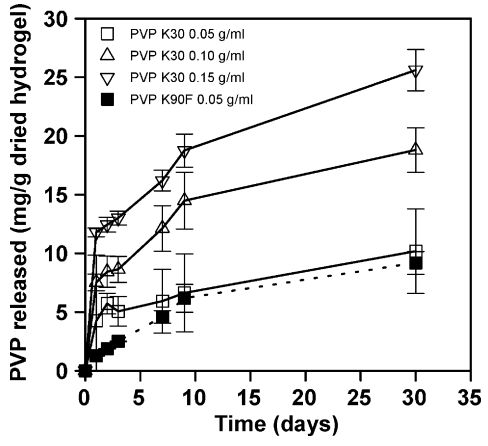

Fig. 5. PVP release profiles from PVP–pHEMA hydrogels prepared with different proportions of PVP (mg/ml) in the absence of water.

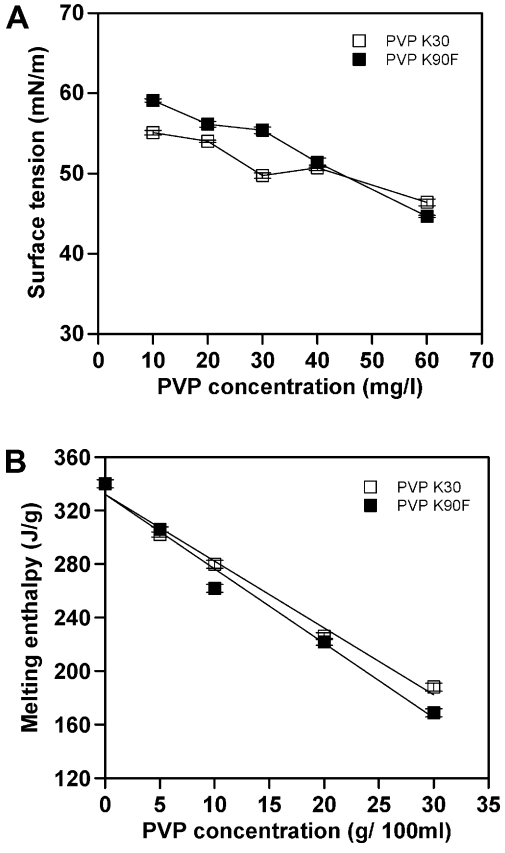

Fig. 6. Surface tension (A) and melting enthalpy (B) of PVP solutions.

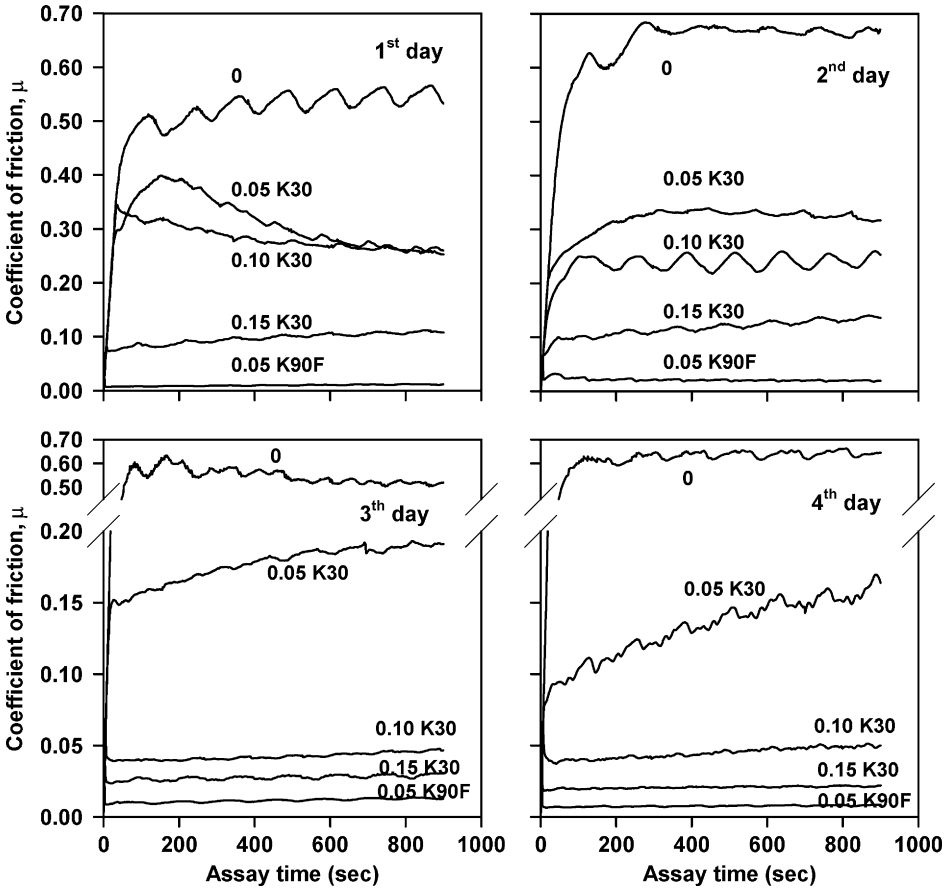

Fig. 7. Coefficients of friction of PVP–pHEMA hydrogels prepared with different proportions of PVP (mg/ml) in the absence of water, after 1-to-4 days of swelling in water.

a non-erodible device. It is known that the release rate of small size molecules (as common drugs) from a conventional soft contact lens occurs quite rapidly and obeys the diffusion laws; the thickness of the lens, its degree of hydration, and the drug concentration in the lens being critical factors [28,29]. The high molecular weight of PVP makes the entanglement of its long chains in the pHEMA mesh possible and hinders the movement of PVP through the network. This explains that its release can be sustained for much longer (beyond 30 days). As it could be expected, the diffusion rate increased as the water content of the lens raised owing to the increase in mesh size of the network.

When PVP is used as demulcent in ophthalmic solutions, its concentration ranges from 0.1% to 2% (i.e. 0.05–1.0 mg per drop) and several applications per day are commonly required [7,8]. The amounts of PVP released by the discs every 24 h were also in the 0.05–1.0 mg range (each disc weighs 60–70 mg). One difference in the role of PVP as demulcent if solutions or lenses were applied *in vivo* would be related to that most volume of the drop is lost due to defense mechanisms of the eye. The sustained delivery from the lens and the prolonged time of permanence in the post-lens lachrymal fluid could greatly enhance both the amount and the residence time of PVP on the ocular surface, as observed for drugs delivered from contact lenses [30]. On the other hand, concentrations of PVP in the range of those released from the hydrogels significantly decreased the surface tension of the release medium (Fig. 6A), which could contribute to the enhancement of the wettability of the contact lenses. This is directly related to the ability to maintain a stable tear layer in the eye and thus is a critical factor for their comfort and *in vivo* performance [31].

3.3. Friction coefficient

The friction test was carried out using a rheometer, which has two main advantages over the commonly used tribometer: (a) the temperature of the sample and of the liquid trapped between the geometry and the solid surface (Peltier plate) can be precisely controlled; and (b) its high sensitivity enables the measuring of the torque of low friction gels [15]. The friction experiments were carried out from dried hydrogels that were rehydrated in water for 1–4 days. The set up consisted of attaching the discs to the upper movable geometry of the rheometer, while 1 ml of the medium in which the disc swelled (and thus released

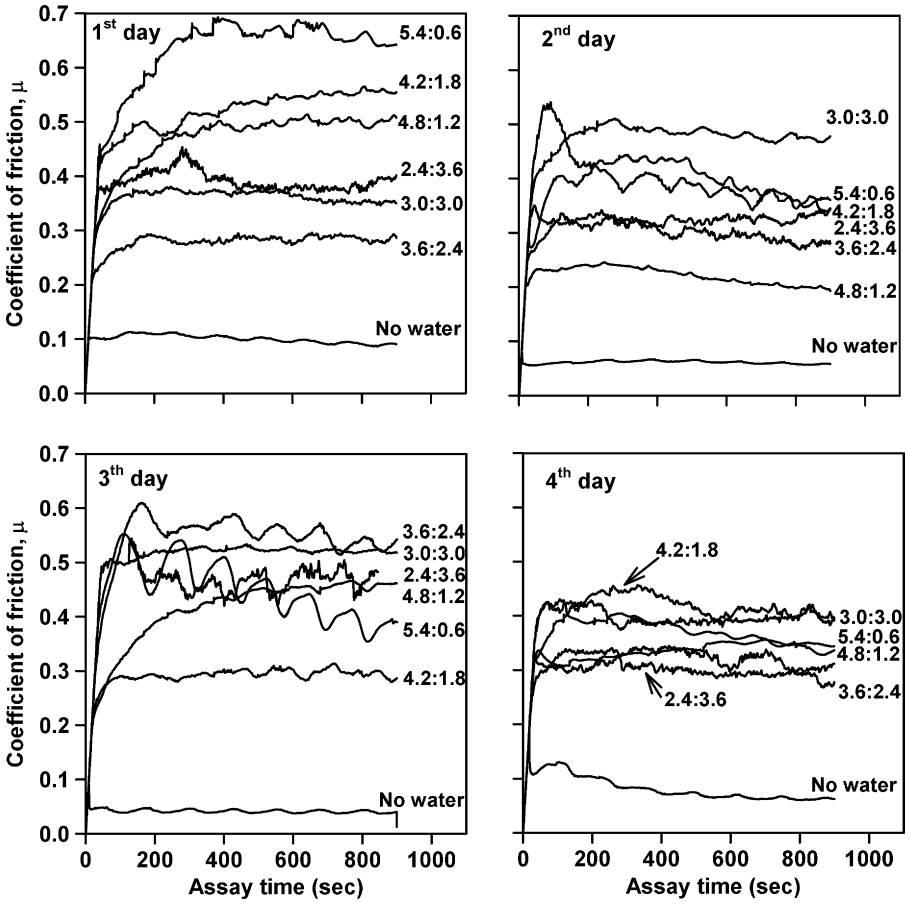

Fig. 8. Coefficients of friction of PVP–pHEMA hydrogels prepared with 0.15 mg of PVP per ml, using different monomer:water ratios, after 1-to-4 days of swelling in water.

PVP) was deposited on the Peltier plate to avoid dehydration of the hydrogel. The use of this medium, instead of pure water, should mimic the *in vivo* situation better. Not only the PVP interpenetrated into the lens and protruded out from the surface, but also the PVP already released from the disc should contribute to the lubricant effect. A minimum of 15 min for conditioning step was necessary to avoid influence of relaxation on the measurement of the friction. The values of the coefficients of friction are shown in Figs. 7 and 8; variability between replicates being below 5%. The results obtained are in the range of 0.02–1.7 previously found for pHEMA hydrogels of various cross-linking densities and hydration degrees intended to be used as synthetic articular cartilage [32].

Regarding hydrogels prepared in absence of water, control pHEMA hydrogel exhibited μ values of around 0.5, which remained constant after 24 h of hydration. By contrast, hydrogels containing PVP K30 showed time-dependent μ values; i.e. they progressively decreased from the 1st to the 4th day. Additionally, the greater the amount of PVP added to the monomer soup, the lower the μ value. As can be observed in Fig. 7, after 3 days of hydration pHEMA hydrogels prepared with 0.10 or 0.15 g PVP (per gram of hydrogel) showed a decrease in μ values greater than 10-fold with respect to control hydrogels. Such a low friction, which is comparable to that found for PVA hydrogels intended for joint lubrication [33], may be due to the contribution of both: (a) the lubrication of the hydrogel–Peltier plate interface by the PVP released from the lens (estimated by simultaneous monitoring of PVP concentration in the swelling medium at the time of the friction experiment; Fig. 9); and (b) the increase in the hydrodynamic solvent layer thickness and the decrease in shear resistance due to that the PVP brushes at the hydrogel surface deform more easily than the cross-linked pHEMA network [15].

The greater lubricious efficiency of PVP K90F was clearly evidenced from the 1st day. This means that an increase in the molecular weight of PVP (in the range evaluated) favorably contributes to making the surface of the lenses more slippery. The greater thickening ability and a slightly greater affinity for water of PVP K90F explain this finding [34]. It was previously reported that highly hydrophylic polymer gels have a low coefficient of friction due to the greatest amount of water that can be sorbed to their structure [35]. DSC analysis of PVP solutions (Fig. 6B) indicated that those prepared with 60% PVP K90F and 40% water have all water as bound water whilst in the case

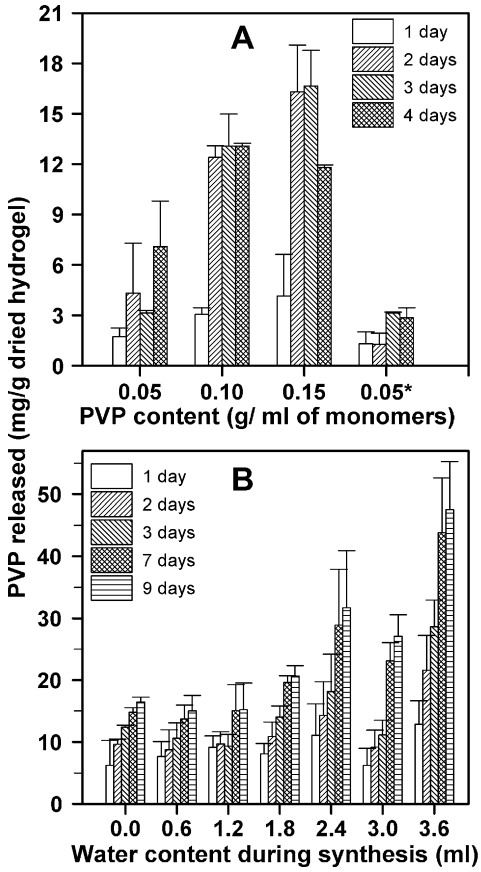

Fig. 9. PVP released from the PVP–pHEMA hydrogels subjected to the friction assay at the time at which the friction coefficient was recorded. (A) hydrogels prepared in the absence of water with different proportions of PVP K30 or 0.05 g/ml of PVP K90F(∗); (B) hydrogels prepared with 0.15 g of PVP K30 per ml and different monomer:water v/v ratios (total volume 6 ml).

of PVP K30 solutions, the maximum content in water for being all as bound water is 33%. Thus, when the disc is pressed during the assay, less water molecules are squeezed out of the hydrogel and more remain attracted to the hydrophilic polymer forming a more efficient lubrication film on the hydrogel–Peltier plate interface.

Hydrogels prepared with PVP K30 (0.15 g/g) in the presence of water also showed a decrease in μ values as a function of hydration time (Fig. 8). After the first 24 h, hydrogels prepared from 5.4:0.6, 4.8:1.2 and 4.2:1.8 had μ values similar to the control pHEMA without PVP. Any hydrogel prepared in aqueous medium with PVP K30 (0.15 g/g) showed greater friction coefficient than the hydrogel prepared with PVP K30 (0.15 g/g) without water. Amongst hydrogels prepared in aqueous medium, increased proportions of water during synthesis slightly decreased the friction, but their μ values were still much higher than those observed for hydrogels prepared with PVP in the absence of water. On the 4th day all porous hydrogels reached similar μ values, despite those synthesized in presence of greater proportions of water released more PVP (Fig. 9). It should be noted that these latter hydrogels also have a more irregular and bumpy surface, which clearly counteracts the lubricant effect of PVP. To sum up, an adequate equilibrium between interpenetrating lubricant agent and surface topology of the lenses is required to achieve a minimum in friction.

4. Conclusions

The results obtained clearly prove that high proportions of PVP can be incorporated to pHEMA-based hydrogels, without compromising their optical clarity, for providing a slow delivery of PVP by diffusion. The adequate choice of PVP molecular weight and of the contents in water and PVP during synthesis may enable to achieve a significant decrease in the surface tension of the aqueous medium surrounding the hydrogels and a marked reduction of their friction coefficients, which are critical factors for the comfort of extended-wear soft contact lenses.

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