

Study of the PVA hydrogel behaviour in 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid

S. Paţachia^{1*}, Chr. Friedrich², C. Florea¹, C. Croitoru¹

¹Department of Chemistry, ‘Transilvania’ University of Brasov, 29 Eroilor Street, 500036 Braşov, Romania

²Freiburg Materials Reserch Center (FMF), ‘Albert Ludwigs’ University Freiburg, Stefan-Meier-Str. 21, 79104 Germany

Received 29 August 2010; accepted in revised form 1 November 2010

Abstract. The present paper aims at studying the behaviour of the poly(vinyl alcohol) [PVA] cryogel in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}]^+[\text{BF}_4]^-$) aqueous solutions with various concentrations. The gravimetric method showed that the swollen PVA cryogels exhibit mechanically active behaviour. PVA cryogels showed shrinking in the presence of ionic liquid (IL), and re-swelling in the presence of distilled water. The re-swelling is not completely reversible, due to the influence of the IL ions on the gel morphology. The Fourier transform infrared (FTIR) spectra have indicated no chemical interaction between the PVA and the studied IL, but highlighted the gel crystallinity change as a function of IL concentration, as well as changes in the bound water amount. Rheological analyses showed dominating plastifying effect of the cation at a lower IL concentration and dominating kosmotropic effect of the anion at a higher IL concentration. A phenomenological kinetic equation that takes into account both fluxes of matters, in and out of the gel, is proposed, explaining the alteration of the gel properties when it comes in contact with BMIMBF₄ solutions.

Keywords: polymer gels, rheology, ionic liquids, poly (vinyl alcohol), 1-butyl-3 methylimidazolium tetrafluoroborate

1. Introduction

The main properties of hydrogels, such as density, sorption and diffusion capacity, mechanical, optical and electrical properties are determined by their water content [1–5]. Hydrogels exhibit a high degree of swelling in aqueous environment. In the presence of organic solvents as well as of ionic aqueous solutions or liquid ionic compounds, the hydrogels could shrink or swell, modifying their water content and, as a consequence, all other properties of the gels [6–10].

The determination of swelling behaviour of hydrogels in different environments is very important due to their very broad areas of application where hydrogels come in contact with organic or inorganic ionic substances, such as: wound dressing, drugs and protein delivery, artificial tissues, muscles or

other organs, separation processes by sorption or diffusion, sensors design etc. [11, 12, 33, 34].

The behaviour of hydrogels with different compositions, in the presence of different ionic substances has been studied [13, 18, 23–25, 32].

PVA is a widely used polymer, due to its exceptional properties such as non-toxicity, non-carcinogenicity, water solubility, biodegradability, biocompatibility, good mechanical and optical properties that could generate hydrogels by physical and chemical ways. Loaded with ionic substances, PVA could be a suitable matrix for electrolytes that could be used in electrochemical systems [14–17].

The electrical stability of these systems is affected by the water (solvent) volatility. The replacement of aqueous or organic solvents of electrolytes that imbibe the PVA hydrogels with room temperature

*Corresponding author, e-mail: st.patachia@unitbv.ro

© BME-PT

ionic liquids (RTIL-s) could be a promising way to obtain solid-like electrolyte materials.

Ionic liquids are ionic substances which contain generally organic cations and inorganic or organic anions, with almost no volatility, high conductivity and exhibit a large electrochemical window. Their non-volatility decreases the electrochemical instability risks caused by the solvent evaporation and also protect the atmosphere, being considered a green solvent.

The development of hydrophilic air-stable imidazolium based RTIL-s have attracted the researchers' interest and studies on the behaviour of some hydrogels in the presence of these RTIL-s have been reported [17].

There are no studies concerning PVA cryogels and imidazolium based RTIL aqueous solutions interaction.

The main goal of this paper is to monitor and to understand the swelling/deswelling behaviour of the PVA cryogels in the presence of $[\text{BMIM}]^+[\text{BF}_4]^-$ and water and to study its effect on the rheological properties of this ternary system.

2. Materials and methods

2.1. Materials

Poly(vinyl alcohol) with a polymerization degree of 900, a hydrolysis degree of 98% and industrial grades was purchased from the Chemical Plant Râşnov (Romania) and used for the preparation of cryogels without being submitted to any purification processes.

1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}]^+[\text{BF}_4]^-$) ionic liquid was purchased from Sigma-Aldrich (Germany). $[\text{BMIM}]^+[\text{BF}_4]^-$ has been used for the preparation of solutions with a concentration ranging from 5% to 100%. Distilled water has been used for the preparation of all ionic liquid solutions.

2.2. Methods

2.2.1. PVA hydrogel preparation

The PVA hydrogels were prepared by repeated freezing and thawing cycles. The hydrogel sample preparation has been started from a 12% PVA solution obtained by mixing a specific amount of PVA powder in a corresponding volume of distilled water, under continuous magnetic stirring, for

3 hours, at a temperature of 80°C. The obtained PVA solution has been chilled to the room temperature and filtered before further usage. Then, it has been molded in a Petri dish and submitted to 3 repeated cycles of freezing at -20°C for 12 hours, and thawing at room temperature for another 12 hours.

The obtained white and opaque PVA cryogel has been immersed in distilled water for 7 days, at room temperature (25°C), in order to allow the swelling of the prepared samples until reaching their swelling equilibrium. The initially obtained PVA hydrogel has a solid matter (dried polymer) content (CS) of 9.78 w%. Each sample has a content of the dried polymer m_x , calculated as $m_{\text{gel}} \cdot \text{CS} / 100$ (m_{gel} is the mass of the sample balanced in water).

2.2.2. Gravimetric study upon shrinking of PVA hydrogels

The completely swollen PVA hydrogel has been cut into circular samples, pre-weighed, immersed in aqueous solutions of $[\text{BMIM}]^+[\text{BF}_4]^-$ with various concentrations (12, 50, 75% and respectively 100%), and stored at room temperature. The ratio polymer: storage solution was 1:100 (mass/vol). At the predetermined period of time (t), the PVA hydrogels have been taken out of the ionic liquid solutions, gently wiped between two filter papers and weighed (m_t) using a Kern ABJ (Germany) balance with a precision of 10^{-5} g. After each weighing process, the PVA hydrogel samples have been immersed back into the same bath. The weighing procedure for the PVA samples and their mass monitoring has been repeated until reaching the shrinking equilibrium.

2.2.3. Re-swelling process study by gravimetric method

The re-swelling capacity of the shrunk PVA hydrogels has been monitored by using the gravimetric methods described in 2.2.2. The PVA hydrogels shrunk in $[\text{BMIM}]^+[\text{BF}_4]^-$ ionic liquid with different concentrations have been immersed in distilled water and weighed at a predetermined time. The weighing procedure has been repeated until the re-swelling equilibrium of the PVA samples has been reached.

2.2.4. Release of [BMIM]⁺[BF₄]⁻ monitoring

PVA hydrogels initially collapsed in the solution of [BMIM]⁺[BF₄]⁻ with concentrations between 12 and 100% have been immersed in distilled water in order to determine the absolute conductivity of the obtained solutions, due to the ionic liquid release from the studied samples. The conductivity measurements have been performed at room temperature, at predetermined time, using a Radelkis OK-112 (Hungary) conductometer. For a set of the studied PVA hydrogels, the conductivity measurements have been performed without refreshing the storage distilled water, while for another set of samples, the distilled water has been replaced periodically, after each measurement, to avoid the contact of the hydrogel with released ions and to ensure the total IL release.

2.2.5. Gels analysis by Fourier transform infrared spectroscopy [FTIR]

The swollen, shrunk and the re-swollen PVA hydrogels (in the same storage water and in the refreshed storage water as we described in 2.2.4) have been subjected to FTIR spectroscopy in the range of 4000 and 600 cm⁻¹, using a Perkin-Elmer spectrophotometer with ATR device. Prior to the measurement, the samples have been vacuum dried overnight, at 40°C, until the constant weight.

The FTIR analysis gave information about the cryogel crystallinity based on the band intensity ratio of 1141 cm⁻¹:1096 cm⁻¹ [19].

The ratio of absorption band intensities of the 1141 and 1096 cm⁻¹ band has been determined for the shrunk PVA hydrogels and the PVA hydrogels re-swollen in non-refreshed and refreshed storage water (as we described in 2.2.4).

2.2.6. Rheological measurements

The rheological measurements have been performed on a Paar Physica UDS200 rheometer, equipped with 25 mm diameter steel plates. The average sample thickness was 1.5 mm. The storage and loss moduli of the collapsed PVA hydrogels have been measured at a constant temperature of 25°C. The samples were stable under shear conditions ($\nu = 1.0$ Hz and $\gamma = 1.0\%$) on a time scale up to 1000 sec. The experiments with deformation amplitude of about 1% were, for all gels, within the linear viscoelastic regime. The immersion solutions

had the following concentrations: 5, 15, 25, 50, 70 and 100%.

3. Results and discussion

3.1. Gels mass monitoring during their immersion in BMIMBF₄ aqueous solutions

By immersing the PVA HG-s, initially balanced in water, in BMIMBF₄ aqueous solutions it could be noticed that the gels shrink. The shrinkage is influenced by the IL concentration (correlated with the water activity) and the contact time.

Figure 1 shows that higher IL concentration and contact time, results in higher hydrogel mass loss and rate of shrinking, as well as in longer time of swelling equilibrium reaching has been noted.

The PVA gel collapse could be explained by the water elimination from the mass of the gels, due to the high osmotic pressure created by IL ions from the contact solution.

The sigmoidal shape of the curve describing the shrinking process for PVA gels immersed in 12% BMIMBF₄ aqueous solution suggests that there are in fact two simultaneous fluxes of matters in the system: one is that of the water leaving the initially swollen gel and the second one is that of the IL ions that diffuse into the gel.

Firstly, due to the osmotic pressure exerted by IL ions outside the gel, the water molecules, more mobile, will diffuse from the gel, determining its mass loss. Later, IL ions, bigger and less mobile, will penetrate the gel network, determining the mass increase.

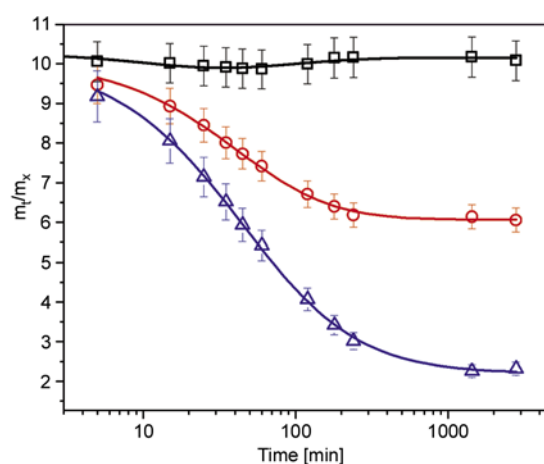


Figure 1. Shrinking process- PVA hydrogel normalized mass dependency as a function of time and concentration of [BMIM]⁺[BF₄]⁻ aqueous solution: (□) 12%; (○) 50% and (Δ) 100% of IL

Once the ionic liquid concentration inside the gel is zero, the osmotic pressure will govern the water release process.

For more concentrated BMIMBF₄ solutions, the higher osmotic pressure within the gel determines a higher and more rapid water release, emphasized by a higher mass loss of the gel. The sorption of IL ions into the gel will diminish, due to the decrease of gel porosity, as a consequence of its collapse. Also, the tendency of IL ions to agglomerate at a higher concentration than 50% [20] could be a cause of their sorption decrease. In this case, the simultaneous processes are less visible on the gravimetric kinetic curves, the IL sorption being negligible by comparison to the water release.

To prove this, PVA HG samples, initially immersed into aqueous solutions of BMIMBF₄, were dried and weighed. The experiments were performed seven times.

3.2. Determination of BMIMBF₄ mass sorbed into the PVA gel

Taking into account the very low volatility of ionic liquids, the amount of BMIMBF₄ sorbed into the gel has been determined as the difference between the mass of the dried gel balanced into the IL solution ($m_{gel,eq,inIL}$) and the mass of the polymer (m_x), calculated taking into account the solid content of the PVA gel balanced in water (Equation (1)):

$$\frac{m_{IL}}{m_x} = \frac{m_{gel,eq,inIL} - m_x}{m_x} \quad (1)$$

It could be noted that the retained amount of BMIMBF₄ decreases when the contact solution concentration increases (Table 1).

In case of the contact between the gel and pure BMIMBF₄, a small negative value for the absorbed

Table 1. BMIMBF₄ mass absorbed into the PVA gel as a function of the IL solution concentration

c _{IL} [%]	m _{IL} /1 g xerogel [g]
0	0
12	0.975649
50	0.702873
75	0.17515
100	-0.01515

IL mass was obtained. This suggests that the usual drying conditions for hydrogels (110°C at normal pressure) are not sufficient to eliminate the bonded water from the gel.

It seems that BF₄⁻ behaves as a kosmotropic ion, interacting with water molecules by H-bondings and structuring them around it. The interaction between BF₄⁻ and water molecules has been reported in the literature by various authors [21]; even other authors calculated the B Jones Dole’s coefficient for much diluted solutions and classified this anion as chaotropic [22]. BMIM⁺, is an organic cation, with a hydrophobic chain, and behaves as a chaotropic ion, breaking the H-bondings between water molecules and PVA-water molecules, transforming initially bonded water in free water. The last one could be easily released from the gel during the drying process. In different papers, it was reported that cation BMIM⁺ behaves as a chaotropic ion while in other situations, it was classified as kosmotropic, due to the possible hydrophobic hydration.

Figure 2. presents the scheme of the processes that take place when PVA HG is in contact with BMIMBF₄.

We could assume that BMIMBF₄ acts as a dehydrating agent for the swollen PVA hydrogels.

This behaviour does not seem to be unique, as similar phenomena have been noted and reported also

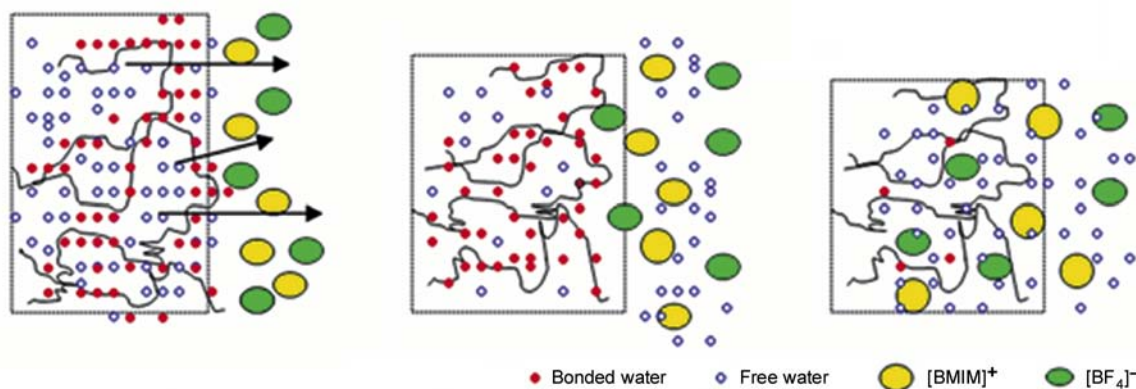


Figure 2. Scheme of the processes that occur at PVAHG contact with BMIMBF₄

for chitosan hydrogels, when in contact with BMIMBF₄ [24]. So, in case the practical interest is to load the PVA hydrogel with BMIMBF₄, we have to use more highly diluted IL solution for the gel immersion. When the hydrogel drying is the goal, it has to be immersed into pure BMIMBF₄.

In Figure 2, we made an attempt to show the mechanism of PVA hydrogel collapse due to the double fluxes of matters in/from the hydrogel. After equilibrium is reached, the collapsed hydrogel contains IL ions embedded into the polymeric network. PVA chains could stronger interact by H bonding between their own OH groups, due to the removal of the bonded water molecules. As a consequence, it is expected that the collapsed gels exhibit a higher modulus.

When the amount of the absorbed IL ions is higher, the effect of the cations on the gel plasticizing has to be more evident. This is valid for the diluted IL solution used for PVA HG immersion.

When the solution concentration is higher, the IL sorption diminishes and the polymer-polymer interaction becomes more dominant. The obtained collapsed gel has to be more rigid.

To prove this assumption, the PVA hydrogels balanced in BMIMBF₄ solutions with different concentrations (Figure 1), have been studied rheologically.

3.3. Rheological analysis of the PVA/BMIMBF₄ gels

Experimental data show, as we assumed, that the PVA hydrogel shrinking in the presence of ionic liquids and the absorption of the ions into the gel matrix strongly influence their rheological properties.

Figure 3 shows that the values of the storage modulus, G' , are higher than that of the loss modulus, G'' , evidencing a solid-like behaviour of the collapsed PVA hydrogels. The plateau modulus, G_p , (determined as the storage modulus at a frequency of 1 Hz), is lower in comparison to the G_p -value of the non-collapsed PVA cryogel, if the concentration of the IL immersion solution is lower than 50% (Figure 4). This behaviour could be correlated with the plasticizing effect of the absorbed cations that is predominant at lower values of the IL concentration, while, at the same time, the volume of the

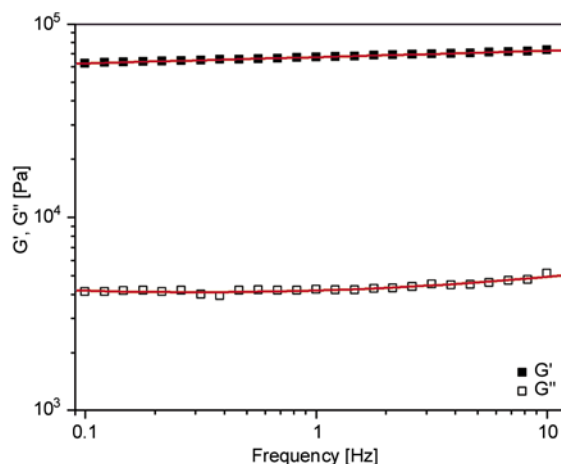


Figure 3. Dependency of the rheological parameters on the frequency, for the PVA hydrogels shrunk in pure [BMIM]⁺[BF₄]⁻

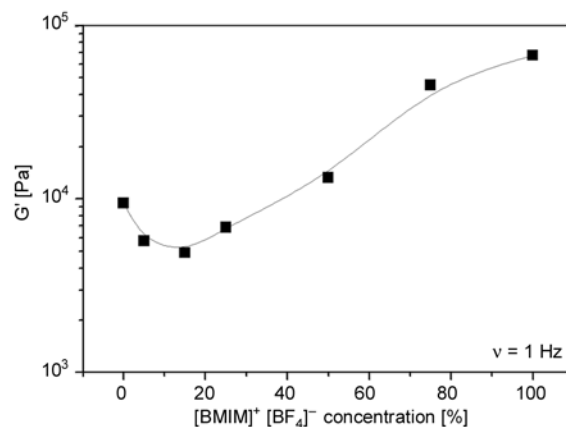


Figure 4. Dependency of the plateau modulus G_p [G' (1 Hz)] on the IL solution concentration

sample is not shrinking significantly in this concentration range.

In the presence of IL having the concentration value between 12% and 50%, the storage modulus of the collapsed PVA hydrogels begins to increase, but its value is still lower than the G_p value corresponding to the initial PVA hydrogel. This behaviour could be correlated to the tendency of IL ions to agglomerate, decreasing the concentration of the free cations [19]. The lower the concentration of the free cations in solution, the lower the cations absorbed and the lower the plasticizing effect marked out.

At a concentration of the IL solution higher than 50%, the storage modulus of the shrunk PVA hydrogels becomes higher than the value of the neat PVA hydrogel. This behaviour could be explained by the increase of the cation agglomeration, which induces the decrease of their absorption and, consequently,

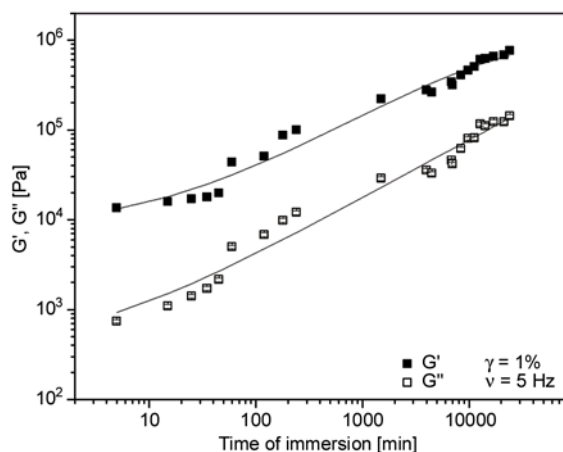


Figure 5. G' and G'' in dependency as a function of the immersion time of the PVA hydrogels in 100% $[\text{BMIM}]^+[\text{BF}_4]^-$

a decrease of the plasticizing effect; additionally, the ions, placed at the interface of the swollen PVA chains, determine a stronger collapse of the studied hydrogel. The PVA hydrogel shrinking is determined by the capacity of the IL ions to extract the water molecules from the hydrogel, expressed by the kosmotropic character of the anions. The elimination of the water molecules from the gel and the higher interaction between the chains of the polymer determines the increase of the gel rigidity. Dynamic moduli G' and G'' of the PVA gels, measured after different periods of their immersion in pure IL, allowed, indirectly, to monitor the sample shrinking (Figure 5).

The variation of the hydrogel rheological properties as a function of the immersion time is consistent with the variation in time of the gel mass, at the sample contact with IL solutions, confirming both matter fluxes: G' , G'' and viscosity increase simultaneously with the gel mass decrease in the first moments after their immersion in $[\text{BMIM}]^+[\text{BF}_4]^-$ solutions. At higher contact times, a relative independence of the rheological parameters on time indicates that the collapse equilibrium is reached.

To check the type of interaction between PVA and BMIMBF_4 the following aspects have been monitored: ILs ions release from the gel, the shrunk hydrogel capacity to re-swell in water and FTIR spectra alteration after gels contact with ILs solutions.

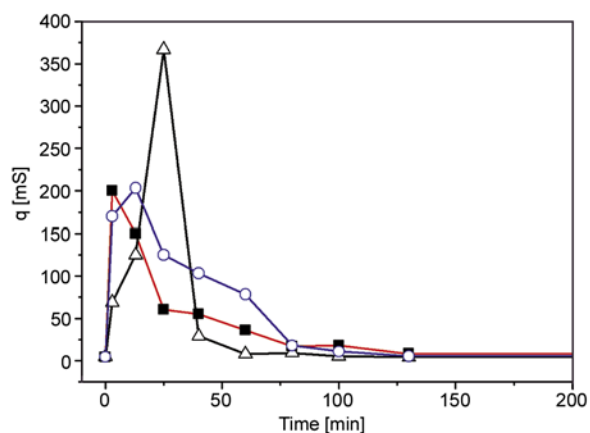


Figure 6. Conductance of the water in which the initially shrunk PVA hydrogels are immersed, as a function of time and of the initial concentration of the IL immersion solution: (■) 12%; (○) 50% and (Δ) 100%

3.4. Monitoring of the BMIMBF_4 release from the gel

The conductometric analysis of the distilled water in which the PVA gels, initially collapsed in IL solutions, have been immersed, shows that the entire amount of sorbed IL is released (Figure 6). This fact emphasized that no chemical interaction between PVA and IL ions occurs.

Also, it could be noted that the diffusion of the ions from the higher collapsed gels is more difficult, the maximum of ions release is being shifted to higher times.

3.5. Monitoring of the gels shrinking reversibility

The recovery capacity of the shrunk PVA hydrogels during the re-immersion into distilled water is confirmed by the increase of their mass. We used refreshed and non-refreshed water to monitor the shrinking reversibility and the results were similar, meaning that the necessary concentration gradient for complete IL removal was ensured.

During the re-swelling process, the samples immersed in 12% IL solution reabsorb water until reaching 99% of the initial PVA hydrogel matrix mass. On the other hand, the PVA hydrogels immersed in pure IL reabsorb water until reaching only approximately 70% of the initial mass of the hydrogels (Figure 7).

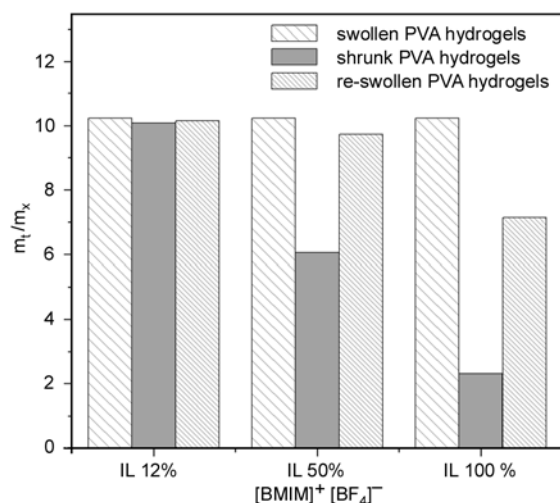


Figure 7. Comparative analysis of the normalized mass of the PVA hydrogels at their initial swollen state, shrunk state and re-swollen state as a function of the IL concentration

The maintenance of the shrunk state of the hydrogels initially immersed in highly concentrated IL solutions evidences a higher interaction between the PVA macromolecular chains by H-bondings. This result is in agreement with the above mentioned data showing that the removal of the bonded water molecules allows stronger interaction between the OH groups of the PVA. That interaction does not seem to be reversible.

3.6. FTIR spectra of PVA/BMIMBF₄ gels

FTIR spectra have been measured in order to clarify the cause of the PVA hydrogel re-swelling limits when they are immersed in water. The absorption bands have been identified [19, 20].

It can be noticed that no new absorption bands appeared in the FTIR spectra, emphasizing that no chemical interaction occurs between PVA and [BMIM]⁺[BF₄]⁻, (Figure 8).

The presence of the IL ions in the gel matrix, proportional to the concentration of the ionic liquid solution, indicates the capacity of the PVA cryogels to retain ions. FTIR spectra of PVA/IL gels evidence the alteration of some absorption bands, both due to the interaction between the components and to changing system composition.

The absorption band from 3270 cm⁻¹ could be attributed not only to the O–H bondings from PVA, but also to those from the bonded water remained into the system after a gel's partial drying. A decrease of the OH band intensity, when the IL con-

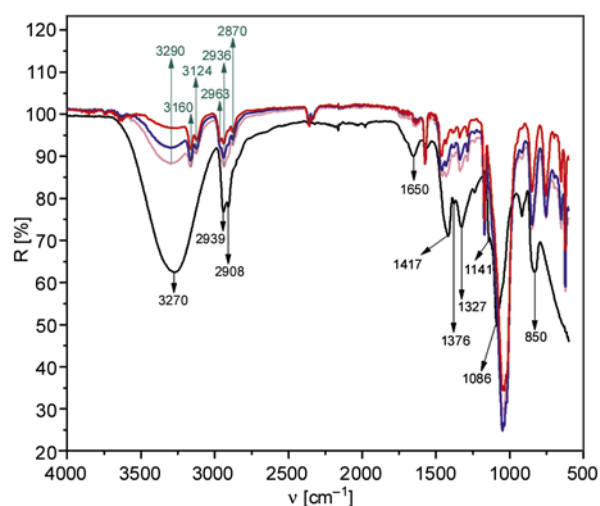


Figure 8. FTIR Spectra of PVA cryogel and PVA cryogels collapsed in IL solutions with different concentrations: 0% IL (—), 12% IL (—), 50% IL (—) and 100% IL (—)

centration into the contact solution increases, was noted. This means that IL ions extract the bonded water molecules from the PVA cryogel matrix. The ratio between the intensity of the bands from 3270 and 2939 cm⁻¹ demonstrates this. The following values were obtained for this ratio: 2.1 (for PVA cryogel), 0.97 (for PVA cryogel immersed in 12% IL solution), 0.68 (for PVA cryogel immersed in 50% IL solution) and 0.44 (for PVA cryogel immersed in 100% IL). The decrease of the mentioned ratio could be attributed simultaneously to the decrease of the bonded water amount but also to the increase of the C–H groups' number into the gel, by BMIM⁺ ions sorption.

The intensity and the width diminution of the band from 3270 cm⁻¹, and its shifting to 3290 cm⁻¹, mean the decrease of the amount of associated OH groups, by H bondings. The shifting of this band could be correlated to the chaotropic character of BMIM⁺ ions, diffused into the matrix, according to the literature [26]. This is consistent with the presence in the FTIR spectra of the shrunk gels, of small absorption bands at 3593 and 3531 cm⁻¹, characteristic for OH free groups [27]. In addition, the characteristic band for [BF₄]⁻ from 1060 cm⁻¹ [27] is split into three peaks and shifted to 1048, 1034 and 1017 cm⁻¹ showing the lowering of B–F vibration symmetry, due to the F atom involving within H bonds with water molecules. Also the skeletal and C–O stretching band from 830 cm⁻¹ from the PVA FTIR spectrum is shifted in the PVA/IL gels spectra

to 844 and respectively 848 cm^{-1} , showing a stiffening of the polymeric chain as a consequence of the interaction by H bondings between OH groups of PVA.

To come to a conclusion, FTIR spectra demonstrate the diffusion of BMIM^+ and BF_4^- ions into the gel and the decrease of the amount of bonded water molecules into the gel as a consequence of the absorbed IL ions that compete for the water molecules binding with PVA.

After re-swelling, the characteristic absorption bands of IL ions disappeared, emphasizing their total release from the gel matrix, in agreement with the conductometric results.

FTIR spectra allow monitoring the PVA crystallinity changes. Figure 9 illustrates the decrease of the PVA cryogel crystallinity when being immersed in ionic liquid solutions. This behaviour could be explained by the strong kosmotropic character of the studied IL that determines the rapid extraction of the water from the gel, and, consequently, leads to the precipitation of the PVA chains in amorphous phase.

The PVA-based cryogel re-swelling leads to the increase of its crystallinity due to the slower release of the IL ions from the matrix and to the kosmotropic effect of the IL ions that structure the water molecules around them; both phenomena allow the macromolecules to organize and to interact by H bonding, determining the increase of the degree of crystallinity.

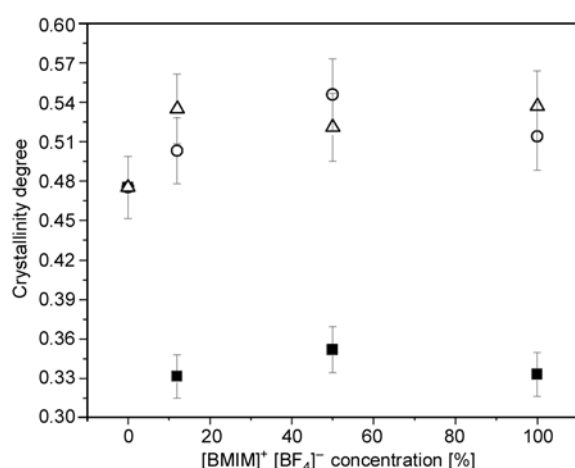


Figure 9. The crystallinity variation of the shrunk and re-swollen PVA cryogels as a function of the initial concentration of the immersion solution: (■) shrunk PVA hydrogels; (○) PVA hydrogels swollen in non-refreshed storage water; (Δ) PVA hydrogels swollen in refreshed storage water

If we consider that the gels density is not significantly affected by the swelling/shrinking processes, and is close to 1 g/cm^3 , it could be noted that after PVA gels immersion in the 50% IL solution, the crystallinity of the gel decreased by approximately 30% while the gels volume decreased by 40%. As a consequence, the increase by approximately 7% of the crystallites concentration/ gel's volume unit has to determine the increase of the shrunk gel modulus. The experimental data show that the modulus increased by 40%. These results evidenced that the amorphous part of the hydrogels plays an important role in the alteration of the PVA hydrogel mechanical properties. In this phase, the PVA chains strongly interact by H bondings as a consequence of the bonded water release, participating in the increase of gel's modulus.

The decrease of the modulus in case of the hydrogels immersed in diluted IL solutions could be determined not only by the plasticizing effect of the BMIM^+ , but also by the possible stronger decrease of the gels crystallinity as compared to its volume decrease.

3.7. Kinetic study of the PVA hydrogels swelling/deswelling

All the above mentioned PVA gel modifications occur during its contact with BMIMBF_4 solutions. Generally, the swelling processes of the gels are described from the kinetic point of view by the Peppas equation [28–31] (Equation (2)):

$$\frac{m_t}{m_x} = k \cdot t^n \quad (2)$$

This equation allows to calculate the exponent n that indicates the water (or other species) diffusion mechanism (Fickian or non-Fickian) and the diffusion constant k . This equation is not applicable in our case, due to the complexity of the process and changing gel morphology. If we still try to apply this equation, we get very low n -values, which do not correspond to the diffusion mechanism.

So, in order to characterize from the kinetic point of view the behaviour of PVA hydrogels in contact with BMIMBF_4 aqueous solutions we propose a phenomenological equation (Equation (3)) that takes into consideration both fluxes of matters. This equation fits very well the experimental data, for both gel collapse and re-swelling.

$$y(t) = \frac{y_0}{\left(1 + \frac{t}{t_0}\right)^p} + y_1 \frac{\left(\frac{t}{t_1}\right)^p}{\left(1 + \frac{t}{t_1}\right)^p} \quad (3)$$

where $y(t)$ is m_t/m_x , t is time expressed in minutes, the values related to the water flux are represented by index 0 and those of the second flux of IL into the gel by index 1, t_0 and t_1 are the characteristic time for which a significant mass change has been noted due to the water or IL flux, respectively, and p is a power law exponent. R is the correlation coefficient.

y_0 shows the swelling equilibrium of the initial gel that is approximately the same for all the samples.

Higher t_0 values for more concentrated IL solutions pointed out that the water release, monitored in the first moments by the osmotic pressure, is counter-balanced by the IL ions sorption on the surface of the gels, leading to an apparent time lag of mass change, determined by gravimetric methods. The higher IL solution concentration is, the greater apparent time lag is, because of the increased amount of the sorbed IL ions.

The increase of t_1 parameter with the IL solution concentration increase shows the extension of the IL sorption to the higher contact times of the IL solution with the PVA cryogel, diminishing the gel weight loss determined by water release. y_1 parameter represents the value of shrinking equilibrium, showing an increase with the IL solution concentration decrease.

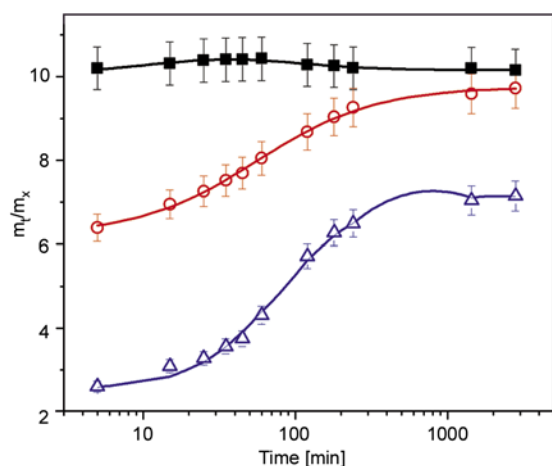


Figure 10. Re-swelling process - variation of the normalized mass of the shrunk PVA hydrogels as a function of time, in distilled water: (■) 12%; (○) 50% and (Δ) 100%

These simultaneous processes emphasized the complexity of the gel collapse in the presence of ionic liquids. The behaviour (mass change as a function of time) of the shrunk PVA hydrogels when they are in contact with distilled water is illustrated in Figure 10.

Experimental data have been fitted by Equation (1). It can be noted that t_0 or/and t_1 increase means more intense simultaneous processes that determine the lowering of the gel mass changing in the first period of the contact time. The higher the IL solution concentration is, the more compact gel result and the lower diffusion rate of the IL ions is observed. As a consequence, higher ‘apparent time lag’ on the re-swelling kinetic curve will be emphasized.

y_0 indicates the initial shrinking equilibrium of the gel and y_1 could be correlated to the equilibrium of the gels in the swollen state.

Although this equation is of entirely phenomenological nature, it allows capturing all details of the shrinking and swelling process qualitatively and it allows a quantitative interpretation of the complex processes going on during the uptake and release of IL.

4. Conclusions

The behaviour of PVA cryogels in the presence of $[\text{BMIM}]^+[\text{BF}_4]^-$ has been studied using a series of analytical techniques. All of them led to the same conclusions, as follows.

In the presence of $[\text{BMIM}]^+[\text{BF}_4]^-$, the swollen PVA cryogels shrink. The higher IL aqueous solution concentration is, the higher shrinking of the PVA gel is. The contact of the PVA gels with lower concentrated IL solutions favored the IL ions sorption. This determines the PVA gels plastisizing, both by their crystallinity decrease and by the dominating chaotropic effect of $[\text{BMIM}]^+$.

At higher IL solutions concentration, the strong collapse of the PVA cryogels determines the decrease of the IL’s ions sorption. In this case, the dominating effect is that of the kosmotropic $[\text{BF}_4]^-$ ions. They determine the transformation of the bonded water molecules in free water molecules, making easier the water release from the gel during the heating. Removing of bonded water determines also a higher interaction between the polymeric chains and as consequence the increase of the gel rigidity.

An equation has been proposed to describe the mass change during the collapse/swelling of the hydrogels in contact with IL solutions and distilled water, respectively, along the entire time domain, until equilibrium is attained. This equation takes into account both fluxes of matters in/from the gel: water flux and IL flux. It emphasizes the swelling and collapse equilibria and the apparent time lag of the gel mass modifying as a function of IL solution concentration. Based on the kinetic curve of shrinking, a mechanism of shrinking/swelling process is proposed.

Acknowledgements

Authors thank The National Council of the Research in Universities (CNCSIS) and the National Authority for Scientific Research for financial support (national grant CNCSIS-IDEI-839/2009). Authors are also grateful for the Erasmus-Socrates European project, which funded travelling and thus allowed interactive collaboration between German and Romanian research teams.

References

- [1] Peppas N. A., Bures P., Leobandung W., Ichikawa H.: Hydrogels in pharmaceutical formulations. *European Journal of Pharmaceutics and Biopharmaceutics*, **50**, 27–46 (2000).
DOI: [10.1016/S0939-6411\(00\)00090-4](https://doi.org/10.1016/S0939-6411(00)00090-4)
- [2] Hennink W. E., van Nostrum C. F.: Novel crosslinking methods to design hydrogels. *Advanced Drug Delivery Reviews*, **54**, 13–36 (2002).
DOI: [10.1016/S0169-409X\(01\)00240-X](https://doi.org/10.1016/S0169-409X(01)00240-X)
- [3] Paţachia S.: Blends based on poly(vinyl alcohol) and the products based on this polymer. in: ‘Handbook of polymer blends and composites’ (eds.: Vasile C., Kulshreshtha A. K.) Rapra, Shawbury, Vol 4A, 288–365 (2003).
- [4] Paţachia S., Rînja M., Friedrich C.: Correlation between poly(vinyl alcohol) cryogel swelling capacity and synthesis parameters. in ‘Recent advances in research on biodegradable polymers and sustainable composites’ (eds.: Jimenez A., Zaikov G. E.) Nova, New York, Vol 3, 121–134 (2008).
- [5] Hassan C. M., Peppas N. A.: Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods. *Advances in Polymer Science*, **153**, 37–65 (2000).
DOI: [10.1007/3-540-46414-X_2](https://doi.org/10.1007/3-540-46414-X_2)
- [6] Lozinsky V. I., Domotenko L. V., Zumbov A. L., Simenel I. A.: Study of cryostructuration of polymer systems. XII. Poly(vinyl alcohol) cryogels: Influence of low-molecular electrolytes. *Journal of Applied Polymer Science*, **31**, 1991–1998 (1996).
DOI: [10.1002/\(SICI\)1097-4628\(19960912\)61:11<1991::AID-APP13>3.0.CO;2-2](https://doi.org/10.1002/(SICI)1097-4628(19960912)61:11<1991::AID-APP13>3.0.CO;2-2)
- [7] Zhang Y., Cremer P. S.: Interactions between macromolecules and ions: The Hofmeister series. *Current Opinion in Chemical Biology*, **10**, 658–663 (2006).
DOI: [10.1016/j.cbpa.2006.09.020](https://doi.org/10.1016/j.cbpa.2006.09.020)
- [8] Shaheen S. M., Ukai K., Dai L., Yamaura K.: Properties of hydrogels of atactic poly(vinyl alcohol)/NaCl/H₂O system and their application to drug release. *Polymer International*, **51**, 1390–1397 (2002).
DOI: [10.1002/pi.1061](https://doi.org/10.1002/pi.1061)
- [9] Paţachia S., Baciú Florea C.: Poly(vinyl alcohol) hydrogels interaction with electrolytes in aqueous solution. *Revue Roumaine de Chimie*, **52**, 1145–1149 (2007).
- [10] Paţachia S., Valente A. J. M., Baciú C.: Effect of non associated electrolytes on the behaviour of poly(vinyl alcohol) based hydrogels. *European Polymer Journal*, **43**, 460–467 (2007).
- [11] Lozinsky V. I., Zubov A. L., Titova E. F.: Swelling behavior of poly(vinyl alcohol) cryogels employed as matrices for cell immobilization. *Enzyme and Microbial Technology*, **18**, 561–569 (1996).
DOI: [10.1016/0141-0229\(95\)00148-4](https://doi.org/10.1016/0141-0229(95)00148-4)
- [12] Lozinsky V. I., Plieva F. M.: Poly(vinyl alcohol) cryogels employed as matrices for cell immobilization. 3. Overview of recent research and developments. *Enzyme and Microbial Technology*, **23**, 227–242 (1998).
DOI: [10.1016/S0141-0229\(98\)00036-2](https://doi.org/10.1016/S0141-0229(98)00036-2)
- [13] Paţachia S., Florea C., Friedrich C., Thomann Y.: Tailoring of poly(vinyl alcohol) cryogels properties by salts addition. *Express Polymer Letters*, **3**, 320–331 (2009).
DOI: [10.3144/expresspolymlett.2009.40](https://doi.org/10.3144/expresspolymlett.2009.40)
- [14] Agrawal S. L., Awadhia A.: DSC and conductivity studies on PVA based proton conducting gel electrolytes. *Bulletin of Materials Science*, **27**, 523–527 (2004).
DOI: [10.1007/BF02707280](https://doi.org/10.1007/BF02707280)
- [15] Hashim M. A., Majid S. R., Ibrahim Z. A., Arof A. K.: Electrochemical double layer capacitor based on cellulose-PVA hybrid electrolyte. *Ionics*, **11**, 464–467 (2005).
DOI: [10.1007/BF02430268](https://doi.org/10.1007/BF02430268)
- [16] Rajendran S., Mahendran O.: Experimental investigations on plasticized PMMA/PVA polymer blend electrolytes. *Ionics*, **7**, 463–468 (2001).
DOI: [10.1007/BF02373585](https://doi.org/10.1007/BF02373585)

- [17] Yang C. C., Lin S. J.: Preparation of alkaline PVA-based polymer electrolytes for Ni-MH and Zn-air batteries. *Journal of Applied Electrochemistry*, **33**, 777–784 (2003).
DOI: [10.1023/A:1025514620869](https://doi.org/10.1023/A:1025514620869)
- [18] Lu J., Yan F., Texter J.: Advanced applications of ionic liquids in polymer science. *Progress in Polymer Science*, **34**, 431–448 (2009).
DOI: [10.1016/j.progpolymsci.2008.12.001](https://doi.org/10.1016/j.progpolymsci.2008.12.001)
- [19] Mansur H. S., Sadahira C. M., Souza A., Mansur A. A. P.: FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. *Material Science and Engineering C: Biomimetic and Supramolecular Systems*, **28**, 539–548 (2008).
DOI: [10.1016/j.msec.2007.10.088](https://doi.org/10.1016/j.msec.2007.10.088)
- [20] Liu W., Zhao T., Zhang Y., Wang H., Yu M.: The physical properties of aqueous solutions of the ionic liquid [BMIM][BF₄]. *Journal of Solution Chemistry*, **35**, 1337–1346 (2006).
DOI: [10.1007/s10953-006-9064-7](https://doi.org/10.1007/s10953-006-9064-7)
- [21] Paṭachia S., Croitoru C., Friedrich C.: Computational study of 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid–water system. in ‘Recent Advances in Mathematical and Computational Methods in Science and Engineering. (MACMESE’08) Bucharest, Romania’ PART II, 469–472 (2008).
- [22] Danten Y., Cabaço M. I., Besnard M.: Interaction of water highly diluted in 1-alkyl-3-methyl imidazolium ionic liquids with the PF₆⁻ and BF₄⁻ anions. *Journal of Physical Chemistry A*, **113**, 2873–2889 (2009).
DOI: [10.1021/jp8108368](https://doi.org/10.1021/jp8108368)
- [23] Zhao H.: Are ionic liquids kosmotropic or chaotropic? An evaluation of available thermodynamic parameters for quantifying the ion kosmotropicity of ionic liquids. *Journal of Chemical Technology and Biotechnology*, **81**, 877–891 (2006).
DOI: [10.1002/jctb.1628](https://doi.org/10.1002/jctb.1628)
- [24] Spinks G. M., Lee C. K., Wallace G. G., Kim S. I., Kim S. J.: Swelling behavior of chitosan hydrogels in ionic liquid–water binary systems. *Langmuir*, **22**, 9375–9379 (2006).
DOI: [10.1021/la061586r](https://doi.org/10.1021/la061586r)
- [25] Rogers R. D., Seddon K. R., Volkov S.: Green industrial applications of ionic liquids. Kluwer, Dordrecht (2003).
- [26] Bridges N. J., Gutowski K. E., Rogers R. D.: Investigation of aqueous biphasic systems formed from solutions of chaotropic salts with kosmotropic salts (salt-salt ABS). *Green Chemistry*, **9**, 77–183 (2007).
- [27] Martens C. F., Schenning A. P. H. J., Feiters M. C., Heck J., Beurskens G., Beurskens P. T., Steinwender E., Nolte R. J. M.: Structure determination, spectroscopic characterization, and magnetic properties of a novel dinuclear copper(II) crown ether bipyridine complex. *Inorganic Chemistry*, **32**, 3029–3033 (1993).
DOI: [10.1021/ic00066a012](https://doi.org/10.1021/ic00066a012)
- [28] Bashir A., Bashir S., Nisa S-U., Huglin M. B.: Chemically crosslinked N-vinyl-2-pyrrolidone/2-hydroxyethyl methacrylate (VP/HEMA) Copolymer for the controlled release of cyclic oligopeptide. *Turkish Journal of Chemistry*, **28**, 279–285 (2004).
- [29] Peppas N. A., Khare A. R.: Preparation, structure and diffusional behavior of hydrogels in controlled release. *Advance Drug Delivery Reviews*, **11**, 1–35 (1993).
DOI: [10.1016/0169-409X\(93\)90025-Y](https://doi.org/10.1016/0169-409X(93)90025-Y)
- [30] Kim B., La Flamme K., Peppas N. A.: Dynamic swelling behavior of pH-sensitive anionic hydrogels used for protein delivery. *Journal of Applied Polymer Science*, **89**, 1606–1613 (2003).
DOI: [10.1002/app.12337](https://doi.org/10.1002/app.12337)
- [31] Ji S., Ding J.: The wetting process of a dry polymeric hydrogel. *Polymer Journal*, **34**, 267–270 (2002).
DOI: [10.1295/polymj.34.267](https://doi.org/10.1295/polymj.34.267)
- [32] Shi J., Guo Z-X., Zhan B., Luo H., Li Y., Zhu D.: Actuator based on MWNT/PVA hydrogels. *Journal of Physical Chemistry B*, **109**, 14789–14791 (2005).
DOI: [10.1021/jp052677k](https://doi.org/10.1021/jp052677k)
- [33] Murali Mohan Y., Keshava Murthy P. S., Sreeramulu J., Mohana Raju K.: Swelling behavior of semi-interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(acrylamide-co-sodium methacrylate). *Journal of Applied Polymer Science*, **98**, 302–314 (2005).
DOI: [10.1002/app.21849](https://doi.org/10.1002/app.21849)
- [34] Sambasivudu K., John P. S., Keshava Murthy P. S., Mani Y., Murali Mohan Y., Sreeramulu J., Mohana Raju K.: Poly(vinyl alcohol) based pH responsive semi-IPN hydrogels: A comparative swelling investigation. *International Journal of Polymeric Materials*, **56**, 1099–1111 (2007).
DOI: [10.1080/00914030701283030](https://doi.org/10.1080/00914030701283030)