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Syneresis and fibrillation of conducting polyaniline gels

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Abstract

The results of the analysis of the morphology of highly conducting polyaniline/*m*-cresol gels are reported. It is shown that the procedure used to prepare gels of conductivities ranging from 3 to 150 S/cm implies: (a) syneresis, associated with phase separation, which is provoked by a lowering of the quality level of the solvent due to absorption of humidity, (b) fibrillar morphology, due to the facility of the stiff, fully protonated, polyaniline chains to be orientated.

Keywords: Conducting gels; Syneresis; Fibrillar morphology

1. Introduction

Polyaniline (PANI) is one of the most promising intrinsically conducting polymers due to its straightforward polymerization, chemical stability and high conductivity. PANI is commonly available as a powder of an emeraldine salt doped with a mineral acid. However, this material is very difficult to process unless it is plasticized with alkyl chains, which requires further chemical work and reduces its conductivity. Following the route developed for other infusible polymers, such as rod-like polymers which give rise to high-modulus fibers based on lyotropic liquid crystals, the use of polyaniline/solvent systems has been considered to overcome this difficulty. Solid films of conductivities above 150 S/cm are obtained from solvent casting [1–4], although their mechanical properties are very poor and hardly useful for practical purposes. On the other hand, gels obtained from polyaniline/solvent systems, showing conductivities no higher than 10^0 S/cm, have been reported in the literature [5–14]. Recently, we have developed a method to obtain PANI gels with conductivities up to 150 S/cm, which differ from brittle films of similar conductivity because of their viscoelastic characteristic response [15]. In this paper, the results of the analysis of the morphology of highly conducting gels, obtained with this new procedure, are reported.

2. Experimental

Following the method described in the aforementioned previous paper [15], polyaniline emeraldine base (PANI), supplied by Panipol Ltd., was dry mixed with camphorsulphonic acid (CSA) at a ratio PANI:CSA 1:0.5 mol/mol and subsequent solutions are prepared by adding doped polyaniline, following denoted as $PANI(CSA)_{0.5}$, to *m*-cresol. The solvent was dried with 0.4 nm molecular sieves and no traces of water were detected by FTIR. Mechanical stirring is carried out in a special blade-vessel system designed to impart high shear rates. The solutions are poured into moulds and submitted to a controlled solvent evaporation process in a climatic chamber, which allows to obtain gels at a range of 5–60 wt% $PANI(CSA)_{0.5}$. It is important to remark that unlike other methods of preparing PANI-based gels [6–8,11–14], our procedure does not require the use of formic acid as a processing medium. The conductivity of the gels was measured using the four point probe method and the dynamic viscoelastic properties in a plate–plate TA instruments CSL 100 rheometer. Micrographs of the gels were obtained by scanning electron microscopy (SEM) using a Hitachi S-270 apparatus.

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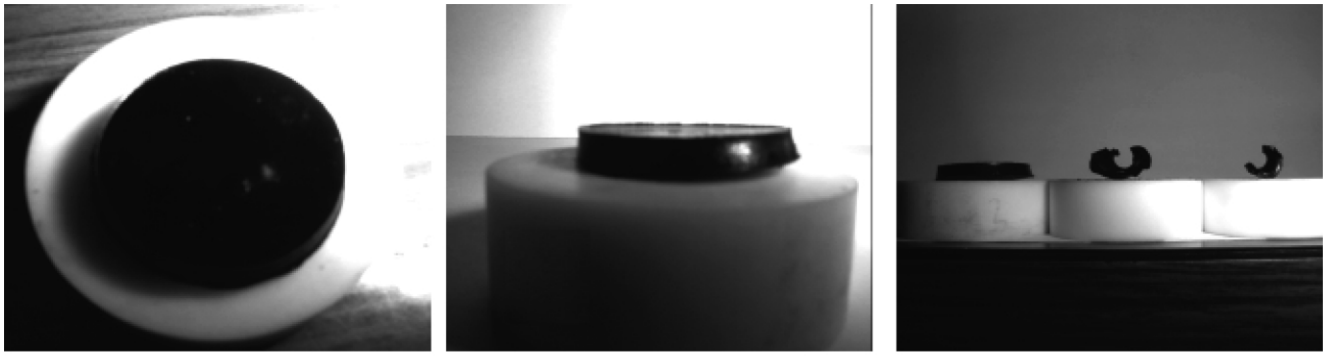

Fig. 1. Shrinkage of the gel network: (a) cylindrical pellet of a 5.4 wt% PANI(CSA)$_{0.5}$ fresh gel (without shrinkage), $\Sigma = 4.7$ S/cm; (b) unsymmetrical contraction at 48 h; (c) macroscopic aspect of a PANI(CSA)$_{0.5}$/*m*-cresol gel in function of ageing time, which increases from left to right leading to an undesirable damage in the gel shape.

3. Results and discussion

Obtaining highly conducting gels implies an ageing process which leads to a dramatic dimensional change associated with the shrinkage of the gel network, as can be seen in Fig. 1. This process, called syneresis, has been widely analysed in the case of inorganic gels, but few papers report on syneresis of organic polymer gels. It is postulated [16] that a phase separation takes place as the polymer chains cluster together creating regions of free liquid. For instance, Hong et al. [17] observe a significant syneresis in poly (vinyl alcohol) (PVA) gels prepared with ethylene glycol (EG), but not in PVA/*N*-methylpyrrolidone (NMP) gels, assuming this result to be due to the lower polymer–solvent interaction of the former. A poor polymer–solvent interaction makes phase separation easier during gelation, which favours syneresis. In our PANI(CSA)$_{0.5}$/*m*-cresol gels, the quality of the solvent is a priori good [1], but it can be reduced because of its hygroscopic nature. Gettinger et al. [18] found that adding water to pre-dried PANI(CSA)/*m*-cresol solutions causes polymer chain to coil. Therefore, the absorption of certain humidity by *m*-cresol during the gel preparation probably triggers the phase separation, which makes the network structure unstable during ageing. As a matter of fact, FTIR analysis of the gels reveals the presence of water, absorbed during gelation process. On the other hand, the mechanical origin of shrinkage or volumetric contraction lies in compressive stresses in the network associated to a negative pressure in the liquid, which arises when liquid evaporates from the gel. As is shown in Fig. 1b, volumetric contraction is not necessarily uniform, which actually is a logical consequence of non-uniform variation in the capillary pressure with position. This local variation of contraction constitutes a problem to obtain samples of hypothetical practical uses since it can lead to a damage of the gel (Fig. 1c). This difficulty can be overcome employing special moulding conditions to perform a uniform contraction during the ageing process [10].

The conductivity of the gels not damaged by non-uniform contractions ranges from 3 to 150 S/cm increasing with concentration following the scaling law $\Sigma \propto c^{1.6}$. The elastic modulus G, which ranges between $7 \times 10^{+3}$ and $5 \times 10^{+5}$ Pa, also scales with concentration, although with a different scaling exponent, $G \propto c^2$.

SEM analysis to obtain micrographs of the gels leads to an original experimental feature: gold coating becomes unnecessary for SEM observations, because of the electrical conductivity of the samples. This is not the case of less conducting PANI gels reported in the literature, which need to be gold-coated to obtain SEM micrographs [12,13]. As can be seen in Fig. 2, SEM micrographs reveal a gel surface full of craters. This porosity must be attributed to the expulsion of the free liquid, associated with the phase separation, during the syneresis. Since this ageing process implies that polymer chains cluster together and considering that PANI is a rigid macromolecule that can be easily oriented, a fibrillar morphology could be expected. This is experimentally confirmed in Fig. 3. Actually the gel preparing method involves pouring the PANI solution into

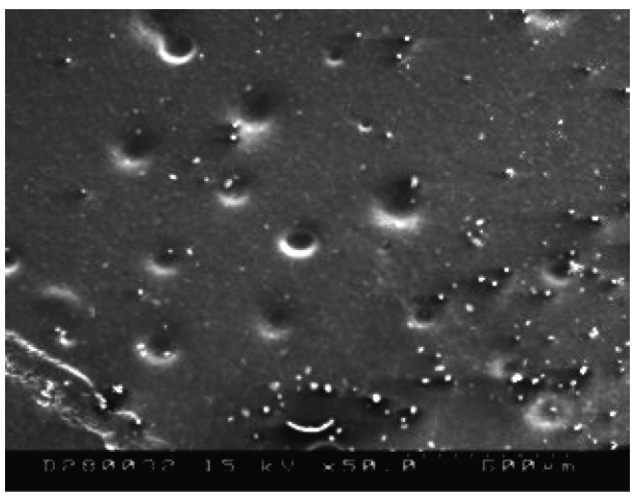

Fig. 2. SEM micrograph obtained from a 2-week aged gel. The porosity of the gel surface is related to the ageing phenomenon called ‘syneresis’.

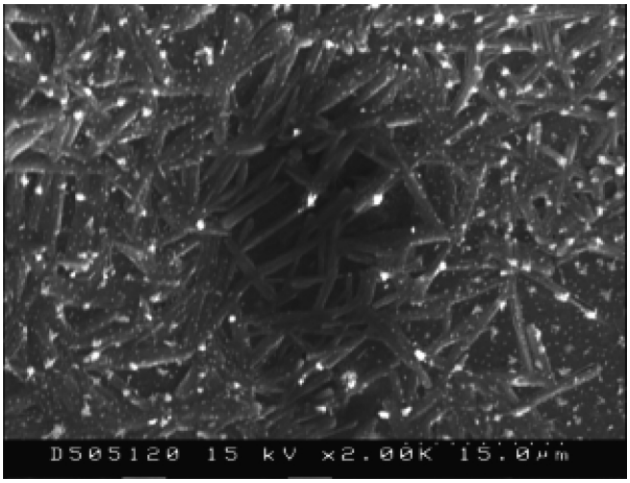

Fig. 3. Scanning electron micrograph of a gel after a very long drying time (several months). It is clear that the network of the gel presents fibrillar morphology.

moulds, which very likely provokes the orientation necessary for fiber formation. Taking into account previous findings with fully protonated PANI in solution [3], the development of a lyotropic liquid crystalline phase during the flow involved in the pouring process must not be discarded. From a more general point of view, the existence of a fiber-like structure is one of the basic characteristics of thermoreversible gels. As an example, Daniel et al. [19] considered the case of syndiotactic polystyrene sPS: sPS/benzene and sPS/toluene systems display a fibrillar morphology and both give rise to gels, while the sPS/*trans*-decaline system exhibits a spherulitic morphology and is not able to constitute a gel. Besides this basic aspect linked to the recognition of a gel, the presence of an interconnected network morphology is a crucial point in order to improve the conductivity of PANI based systems [12,13,20,21]. In the case of films obtained from solutions of PANI–dinonylnaphthalene sulfonic (DNNSA) in xylene, Kinlen et al. [20] observed small islands of conducting PANI imbedded in a non-conducting amorphous dopant matrix giving rise to conductivities in the range of 10^{-6} S/cm. Treatment of PANI-DNNSA with surfactants such as benzyltriethylammonium chloride produces a remarkable conductivity enhancement (up to 5 orders of magnitude) due to self assembly of PANI–DNNSA molecules into an interconnected network morphology. A Similar conclusion about the effect of morphology on conductivity is drawn by Jana and Nandi in their peculiar PANI–sulphonic acid dopant systems [13], defined as 'gels without a liquid': the maximum conductivity corresponds to PANI weight fraction 0.22 to 0.4 (depending on the dopant) in which a fibrillar morphology is observed. No fibril is formed for compositions above 0.60 PANI, probably because of lack of complete doping of PANI with the sulphonic acid dopant. These authors comment on the role played by formic acid (as a processing medium) acting as a coagulant to produce fibrils. In the light of this, we have to remark the fiber forming easiness inherent to our new method for gel preparation, which avoids the use of formic acid and leads to conductivities 50 times higher than previous results [15].

4. Conclusions

In summary, the procedure used to prepare the PANI$(CSA)_{0.5}$/*m*-cresol gels implies: (a) syneresis, associated with phase separation, which is provoked by a lowering of the quality level of the solvent, (b) fibrillar morphology, due to the facility of the stiff PANI-CSA chains to be orientated.

Both analysed morphological aspects, syneresis and fibrillar network, have a crucial importance, for the good and for the bad, in the potential use of the investigated systems for practical purposes.

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References

[1] Cao Y, Smith P, Heeger AJ. Synth Met 1992;48:91–7.
[2] MacDiarmid AG, Epstein AJ. Synth Met 1994;65:103–16.
[3] Cao Y, Smith P, Heeger AJ. Synth Met 1993;55–57:3514–9.
[4] Ikkala OT, Pietilä LO, Ahjopalo L, Österholm H, Passiniemi PJ. J Chem Phys 1995;103(22):9855–63.
[5] Tzou K, Gregory RV. Synth Met 1993;55-57:983–8.
[6] Vikki T, Ruokolainen J, Ikkala OT, Passiniemi P, Isotalo H, Torkkeli M, Serimaa R. Macromolecules 1997;30:4064–72.
[7] Vikki T, Isotalo H, Ruokolainen J, Passiniemi P, Ikkala OT. Synth Met 1999;101:742–5.
[8] Ikkala OT, Vikki T, Ruokolainen J, Hiekkataipale P, Passiniemi P, Mäkelä T, Isotalo H. Mater Res Soc Symp Proc 1998;488:377–82.
[9] Santamaria A, González I, Lizaso E, Muñoz ME, Pomposo JA, Grande H. Proc Int Congr Rheol 13th 2000;376.
[10] González I. PhD Thesis, San Sebastián: UPV/EHU, in progress.
[11] Tiitu M, Hiekkataipale P, Hartikainen J, Mäkelä T, Ikkala OT. Macromolecules 2002;35:5212–7.
[12] Jana T, Nandi AK. Langmuir 2000;16:3141–7.
[13] Jana T, Nandi AK. Langmuir 2001;17:5768–74.
[14] Jana T, Chatterjee J, Nandi AK. Langmuir 2002;18(15):5720–7.
[15] González I, Muñoz ME, Santamaria A, Pomposo JA, Grande H, Rodríguez-Parra J. Macromol Rapid Commun 2002;23:659–63.
[16] Brinker CJ, Scherer GW. Sol–gel science: The physics and chemistry of sol–gel processing. San Diego: Academic Press; 1990. p. 373.
[17] Hong P, Chen J, Wu H. J Appl Polym Sci 1998;69:2477–86.
[18] Gettinger CL, Heeger AJ, Pine DJ, Cao Y. Synth Met 1995;74:81–8.
[19] Daniel C, Dammer C, Guenet J. Polymer 1994;35(19):4243–6.
[20] Kinlen PJ, Liu J, Ding Y, Graham CR, Remsen EE. Macromolecules 1998;31:1735–44.
[21] Titelman GI, Siegman A, Narkis M, Wei Y. J Appl Polym Sci 1998; 69:2205–12.