AQUEOUS SOLUTION DISTRIBUTED SENSOR EMPLOYING P(BUTYL ACRYLATE-CO-METHYL METACRYLATE-CO-SODIUM ACRYLATE) P(BUA-MMA-C-NaA) COPOLYMERS

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1.- Introduction. In this work, a new sensor based on a specially designed P(butyl acrylate-co-methyl methacrylate-co-sodium acrylate P(BUA-MMA-C-NaA) copolymer**,** which has the following characteristics:(i) it have an anphyphylic nature, presenting a hydrophilic face grafted to an hydrophobic face; (ii) this permits to have a molecular network that avoids its dissolution in almost any liquid (polar or non-polar); (iii) the P(BUA-MMA-C-NaA) copolymer is easily processed to extrude in length continuous cables, which permits the production of actual distributed sensors of several kilometers long; (iv) also, it is straightforward synthesized by emulsion polymerization which permits to obtain inexpensively. The sensors prepared with this polymer have the following features; (i) rapid reaction to the presence of the water contained in aqueous solutions; (ii) mechanical toughness; (iii) and capacity to pinpointing leakages. The electronic system with which they work was developed with very simple technology. The production of actual distributed sensors, of several kilometers long, may survey aqueous leakages or filtrations in a number of industries as; food companies (milk, bear, wine, soft drinks), cleaning and self care products, etc.

2. Sensor design. Fig. 1 shows the main features of the sensor disclosed in this paper. Fig. 1a shows the geometry utilized in all the laboratory tests, while Fig. 1b shows the sensor in an adequate embodiment for field heavy duty. The difference is an external foam coating, permeable to water, that protect the sensor of ground humidity. In order to fulfill the objective listed in Section 1, we designed our distributed sensor with two electrical conductors isolated by PVAm–Cu complex. One conductor is running along the central axis of the cylindrical-shaped polymer, while the other is a helix, in tight contact with the external surface of the polymer

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cylinder. The forming of such geometry is readily managed providing the polymer can be extruded continuously around the axial wire, while the helix is simply wound on the cylinder with a controlled force. A section of the sensor, and associated circuits, is shown in Fig. 2. It is important to mention that this sensor is designed to be installed in double-wall pipes, especially inside the interstice between the walls. However, for single-wall pipes installed outdoors it is necessary lining the pipe with a polyethylene foil and putting on the sensor in between, in order to protect it from the rainwater. If a leakage occurs at any point of the pipe and water suddenly flows, the sensor cable is wetted in this location (point W) and the local polymer resistance is reduced, as a result a fraction of total current, iP, is conducted through the polymer by means of ionic transport to the internal copper wire. On the wetted zone, WPC, a current partition process is developed.

This sensor employs a cross-linked hydrophilic polymer. Also, since the electrical conductivity of water is low when it is pure [10], and unpredictable in case of salts content, the polymer should contain within its bulk a sufficient density of charge carriers, typically ions. The requirements indicated above concerning the properties of the sensitive material constitute a specification list that guided the choice of polymer. Evidently, no commercial material possesses, in its regular form, all the desired characteristics. For this reason, in this work, we developed an original treatment to be applied to a polymer with available grade. In order to obtain materials with such functionalities, new polymers can be employed. Poly(vinyl amine) (PVAm) is a polymer with interesting properties. When softly cross-linked it becomes a hydrogel that is capable of absorbing a large quantity of water without dissolving.

The cross-linking method [11] is based on a copper ion, Cu^{2+}, the complex bonds formed between theCu^{2+} ions and the amine groups of PVAm produce chain junctions in limited density [12], thus interesting properties such as: (i) considerable swelling while absorbing water, (ii) resistance to dissolution in water, (iii) capability of processing by extrusion(iv) excellent thermal and chemical stability, and (v) high electric conductivity in the wet state, are obtained simultaneously.

3. Experimental. In order to evaluate the pinpointing accuracy of the distributed sensor, a sample of 50m in length was connected according to scheme in Fig. 2a; the equivalent circuit for this arrangement is shown in Fig. 2b. The sensor sample was prepared employing copper wires and formulation A as sensor material. The extrusion process was realized employing a laboratory extruder Brabender®. A series of experiments were carried out according to scheme shown in Fig. 2, two Agilent® 34401A multimeters and a power supply Tektronix PS280 were employed. The sensor cable was dried and its humidity stabilized to 25% RH (at 25 ◦C) before each test. Successive test were performed wetting the sensor cable on the points described in Table 2, the wetted zone was of approximately 3 cmin length. The measures were performed employing an electrical potential constant equal to 1V and operating on steady state condition. In order to evaluate the hysteresis level, water absorption–desorption experiments (wetted–dried) were performed. One sensor cable section with length equal to 30cmwas subject to resistance measures in a humidity controlled chamber (Thermotron® 13100A). Initially, the sensor cable was placed in an environment

When electrical resistance attained the steady state, water was poured on the sensor, staying in contact about 10 min (absorption), subsequently the water was removed and the sensor was dried (desorption) by mean of natural convection inside chamber at conditions described above. Finally, the previous sample subjected to absorption–desorption experiments was analyzed by electron scanning microscopy (SEM, Jeol model JSM 5800-LV).

4. Results and discussion. After drying the material obtained was extruded to fabricate the type I and II samples described in the experimental section. It is important to note that commercial hydrogels, which are crosslinked by covalent bonds, are damaged by temperature and shear stress during extrusion. Actually, those hydrogels cannot flow in an extruder without major degradation, because the cross-linking bonds between the polymer molecules are first order bonds, normally covalent, and they are not reestablished after heating or flow. Therefore, the reticulated network is destroyed when it is heated and forced to flow. However, in the present case the bond produced by chelation is a second order bond, which may be reestablished after thermal activated flow. Therefore, when the material is heated, the free volume between molecules increases and their interaction with the copper ions diminish permitting their flow. But, when the material is cooled the free volume diminishes regenerating a new reticulated network and, as a result, the crosslinks strength is reestablished. In order to evaluate the veracity of the previous assumption, we have evaluated the gel fraction before and after the extrusion process at 140 ◦C. The results are reported in Table 3 (in this table also the water uptake and cross-linking density of the formulations after processing are reported).

It is important to observe that the gel fraction obtained is practically the same before and after extrusion. This fact shows that actually the chelating bonds are recovered after a thermal activated flow in an extruder. This characteristic makes this type of cross-linking ideal to produce hydrogels suitable for processing by standard methods (extrusion, injection, etc.)

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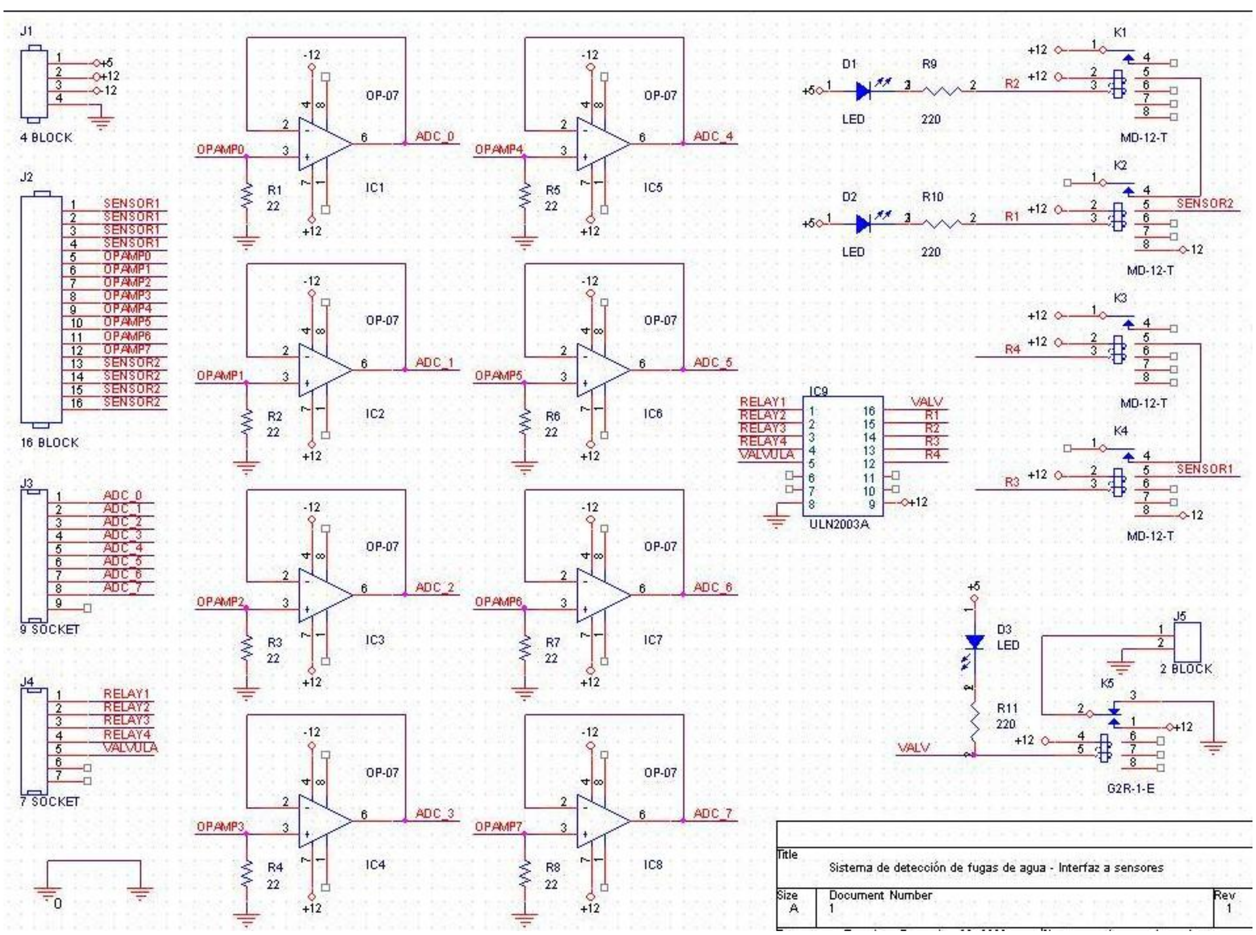
5. Conclusions. The water sensor prototype presents a very short response time and an acceptable accuracy on the pinpointing of water leakages. Its fast electrical response is attributed to diffusion and capillary water absorption process through micro porous structures generated during extrusion process. This phenomenon was confirmed by microscopy analysis (SEM). Besides, the absorption water mechanism evaluated by swelling tests suggests a non-Fickian diffusion process. Finally, the reticulation method of PVAm employing Cu(II) as cross-linking agent allows obtaining polymer material with satisfactory thermal stability and rheological behavior for extrusion processing. This characteristic allows the production of a sensor cable with micro porous morphology that promotes water transportation by capillary diffusion, reducing its response timewhen it is exposed to water. The sensor developed is capable to detect and localize water leaks in a number of pipelines networks in metropolitan areas or in industrial facilities, very fast and precisely.



Esquemático 1