

Characterization of a Superabsorbent Polymer

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ABSTRACT: We studied an amorphous polymer superabsorbent, able to absorb until 1000 times its weight of water. It is consisted of macromolecular chains, dependent between them by chemical bonds. The swelling of the product in the presence of water gives rise to a polyelectrolytic gel. The chemical analysis of polymer by energy dispersive spectrometry and photoelectrons spectroscopy with a microsunder X showed that the product is homogeneous. It contains carbon, oxygen, and sodium. The measurements of specific surface of the product show that the polymer is nonporous and present a weak surface of

about 2.1 m²/g. The thermal study of polymer showed that, under the effect of the temperature and with atmospheric pressure, the polymer is degraded only at temperatures higher than 200°C and becomes porous. When the material is heated at higher temperature of 200°C, its surface becomes increasingly porous with also an increase in the size of the pores. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 782–786, 2007

Key words: polymer; superabsorbent; gel; characterization; heat; water; temperatures; macromolecules

INTRODUCTION

At rest, the chemical gel is presented in solid form.¹ It becomes deformed easily under the action of a constraint. It consists of macromolecular chains assembled in a three-dimensional network. The meshes of the network can adopt a great number of conformations, which confer on the gel, in particular elastic properties, of which the most remarkable aptitude to undergo great deformations. The study of the swelling gel, which has an ordered molecular structure, by absorbing water using diffraction X-rays,^{2,3} makes it possible to notice that the swelling of the polymeric network involves a disorder macromolecular chains.

The polyelectrolytic gel also has strong capacities for the absorption of liquid water.⁴ The study of this gel by the neutron diffusion showed that the appearance of the strong electrostatic interactions, towards the raised rates of swelling, involves an expansion of the polymeric networks. The superabsorbents polymers are classified among the macromolecules gel with permanent junctions.^{5–7} They consist of macromolecules (gelling) connected between them by chem-

ical bonds. In dry material, these polymers are in solid state. In the presence of water, the carboxyl group is ionized and the polymeric system inflates under the effect of the osmotic pressure and gives a polyelectrolytic gel.⁸

The experimental techniques used to characterize neutral polymers are difficult to implement.^{9–11} Indeed, the diffusion properties of polymer, which inflates by absorbing solvent, can vary according to the time and from the change of the structure of polymer during swelling. For the ionic gel, the rate of absorption becomes very high,¹² what involves an additional complication of the swelling system.

EXPERIMENTAL

Equipment

The photographic images were carried out by a sweeping electron microscope with standard JSM-6400F. The composition images were obtained by retromagery of anhydrous polymer (vacuum thorough during 24 h). For the chemical analysis of polymer, we have employed energy disperse spectrometry (EDX) with a microsunder X (OXFOR). We have also employed electronic spectrometry XPS (with an apparatus SIA 100) to extract the quantitative measurements of certain chemical elements and to identify the chemical state of these elements. To complete the chemical analysis of polymer, we have carried out experiments by infrarouge (IR) using an apparatus FTIR Spectrometer: PERKINELMER 1725X. The mea-

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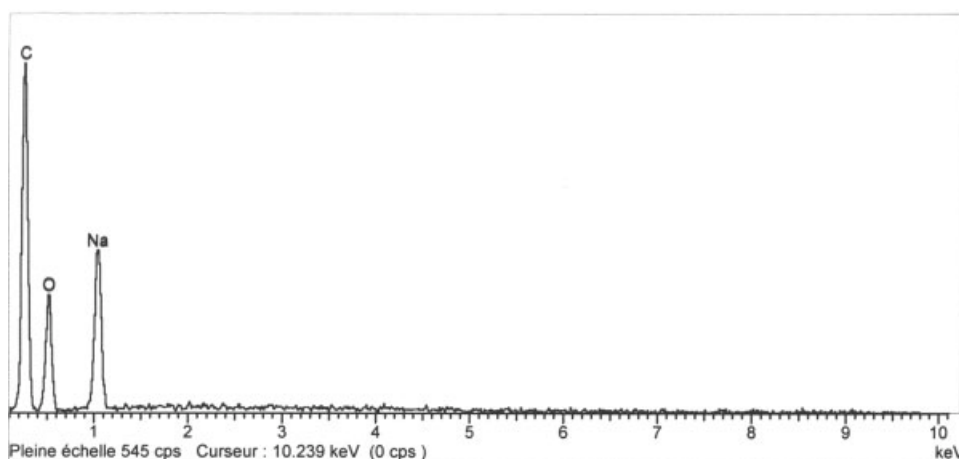


Figure 1 Spectrum obtained by energy disperse spectrometry relating to anhydrous polymer.

measurements of the heat capacities of polymer were taken by differential scanning calorimetry (DSC) with sweeping. The calorimeter used in this study is of type METTLER DSC 12 E. From the diagrams obtained, we can determine at the same time the heat put in place during transformation and to follow the change of the temperature of sample during heating.

Sample

The examined product is a superabsorbing polyelectrolyte (polymer X10). This powder is prepared from the acrylic acid. It is presented in the form of small deformed spherical balls whose diameter varies between 10 and 100 μm . The anhydrous product is amorphous. It is able to absorb up to 1000 times its water weight. Indeed, in the presence of liquid water, the polymer inflates instantaneously and quickly to give rise to a polyelectrolytic wet and transparent gel.

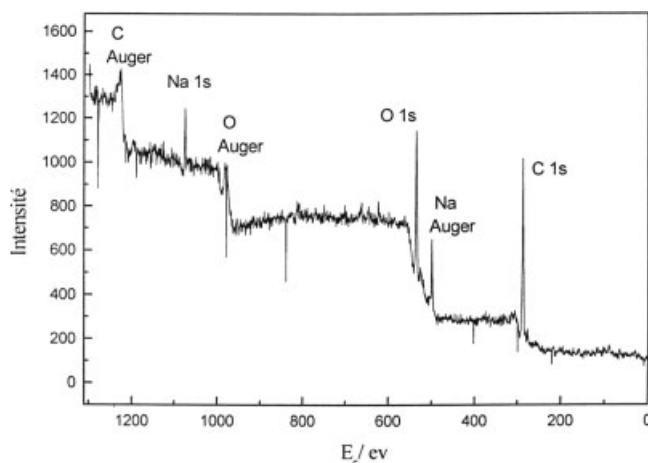


Figure 2 Photoelectrons spectroscopy analyze of polymer.

RESULTS

Chemical analysis of the anhydrous product

We carried out photographic images of polymer by secondary imagery. With this technique, we can see the surface aspect of the sample (Fig. 5). It is based on analyzing secondary electrons emit by the sample at the time of its exposure to an electron beam. We also carried out the composition images by retroimagery of anhydrous polymer (vacuum thorough during 24 h). The latter is based on the detection of the retrodiffrused electrons, when the sample is exposed to an incidental electron beam. It is then possible to distinguish by imagery the different elements of atomic number.

For microanalysis-X of polymer, we have employed disperse spectrometry in energy (EDX) with a micro-sounder X (OXFOR). Figure 1 shows one of the spectra carried out by EDX. The analysis of the spectra obtained for anhydrous polymer shows that the product contains carbon, oxygen, and sodium. The percentage of carbon is overestimated but in more of carbon constituting the sample; the polymer was carbonaceous, so that it is conductive. The light elements, such as hydrogen and nitrogen, cannot be detected by this method. Also, the elements of which the mass percentage is lower than 1% will not be detected. The peak with 0, which appears on the spec-

TABLE I
Results Obtained by the Photoelectrons Spectroscopy Analysis of the Polymer

Element	Energy (eV)	FWHM (eV)	FSR	Aire	% Concentration
Na 1s	1072.5	2.30078	3.52	1629.3	0.92
O 1s	533.5	3.68698	0.57	6343.8	22.12
C 1s	285.7	2.35889	0.15	5819.6	76.96

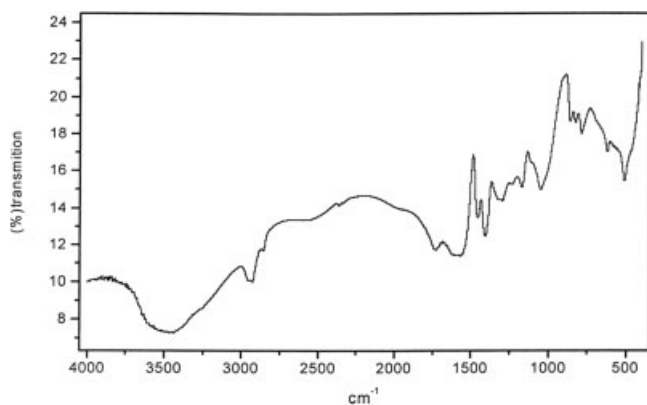


Figure 3 Infrared spectrum of polymer.

trum, is a peak relating to the detector. The analysis of the spectrum of X-rays diffraction obtained for anhydrous polymer shows that the product is amorphous.

Figure 2 shows the spectrum relating to polymer obtained by electronic spectrometry. According to this figure, we can say that the sample is consisted of carbon, sodium, and oxygen. Table I shows the results obtained for polymer.

Figure 3 shows one of the spectra IRs obtained for polymer. We can say that all what is lower than 1000 cm^{-1} corresponds to the clean structure of the polymer (symmetry). The wide strip, which exists between 4000 and 3000 cm^{-1} , corresponds to water. The analysis of all the spectra obtained makes it possible to lead to the results gathered in Table II.

Thermal stability of polymer

The study of thermal stability of polymer was carried out by sweeping DSC under air. The heating of the sample was carried out with various speeds of heating. The analysis of the diagram obtained (Fig. 4) shows that the polymer presents a first endothermic loss (absorbing 77 J/g) starting from a sample temperature of 60°C . After this dehydration, the color of polymer remains white. The second loss, but exothermic (releasing 3.2 J/g), takes place towards 220°C . The color of polymer becomes maroon. The latter

TABLE II
Results Obtained Starting from the Analysis of the Spectra Infrared

Bands (cm^{-1})	Liaison nature
666–875	C–H
1040–1290	C–O
1395–1437	CH sp^3
1470–1604	C=C
1708	C=O
2802–2937	C–H sp^3
3490	O–H

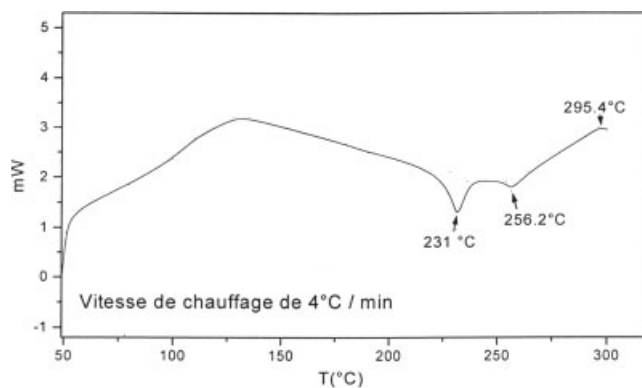


Figure 4 Effect of the temperature on polymer under atmospheric pressure.

loss, exothermic (releasing 3.4 J/g), starts at 250°C . The color of end product is black. Table III lists out the values of the heat capacities of polymer obtained by DSC.

DISCUSSION AND CONCLUSION

The photographic images obtained by secondary imagery show that the polymer is presented in the form of deformed spheres (Fig. 5), which was not the case of the X5 polymer formed by spherical balls.¹³ The surface aspect appears nonporous (Fig. 6), as that was obtained by the method of specific surface measurements of the product, which showed that the polymer is nonporous and present a weak surface ($2.1\text{ m}^2/\text{g}$).¹⁴ The analysis of the composition images obtained by retroimagery made it possible to conclude that our sample is homogeneous.

The spectra carried out by EDX (Fig. 1) show that the product contains carbon, oxygen, and sodium. The presence of sodium in the sample is awaited, since to increase the ionization level of polymer it is necessary to move the acid–basic balance of the acrylic acid towards the basic form and this is possible with the NaOH addition.

The analysis of the spectrum of X-rays diffraction obtained for polymer shows that the product is amorphous. That was also obtained of the study of the X5

TABLE III
Results Obtained for the Thermal Stability of Anhydrous Polymer

C_p ($\text{J/g } ^\circ\text{C}$)	Initial temperature ($^\circ\text{C}$)	Final temperature ($^\circ\text{C}$)	Polymer nature
0.88	50	80	Hydrated
1.13	80	110	Hydrated
1.28	110	140	Hydrated
1.35	140	170	Lowly hydrated
2.05	170	200	Anhydrous

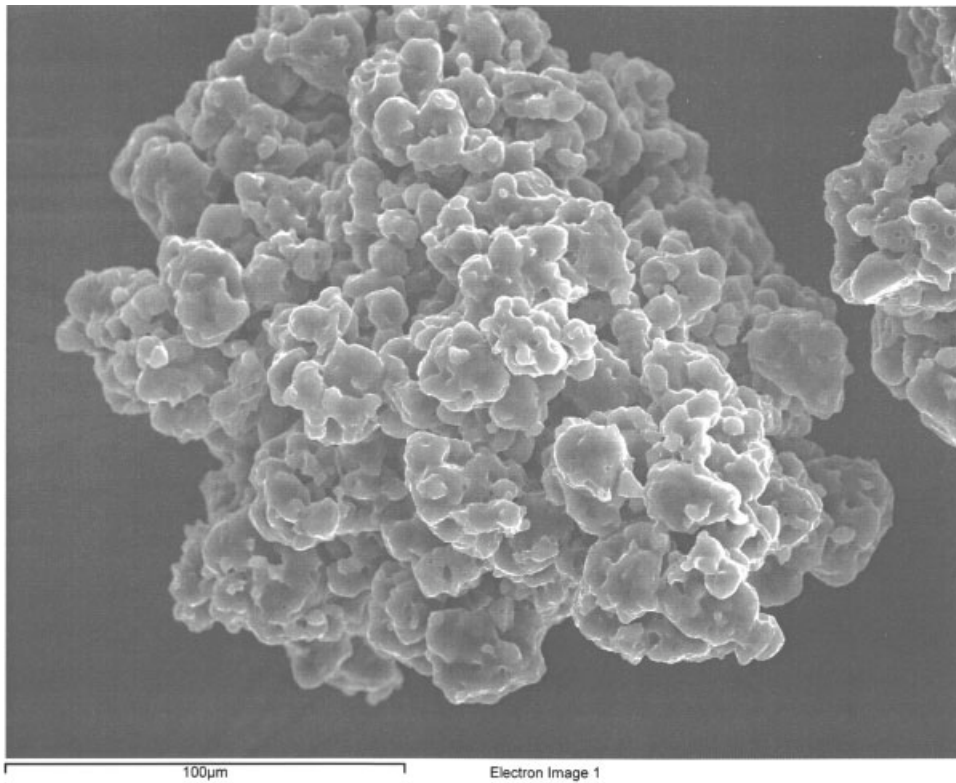


Figure 5 The surface aspect of the anhydrous polymer seen under the sweeping electron microscope.

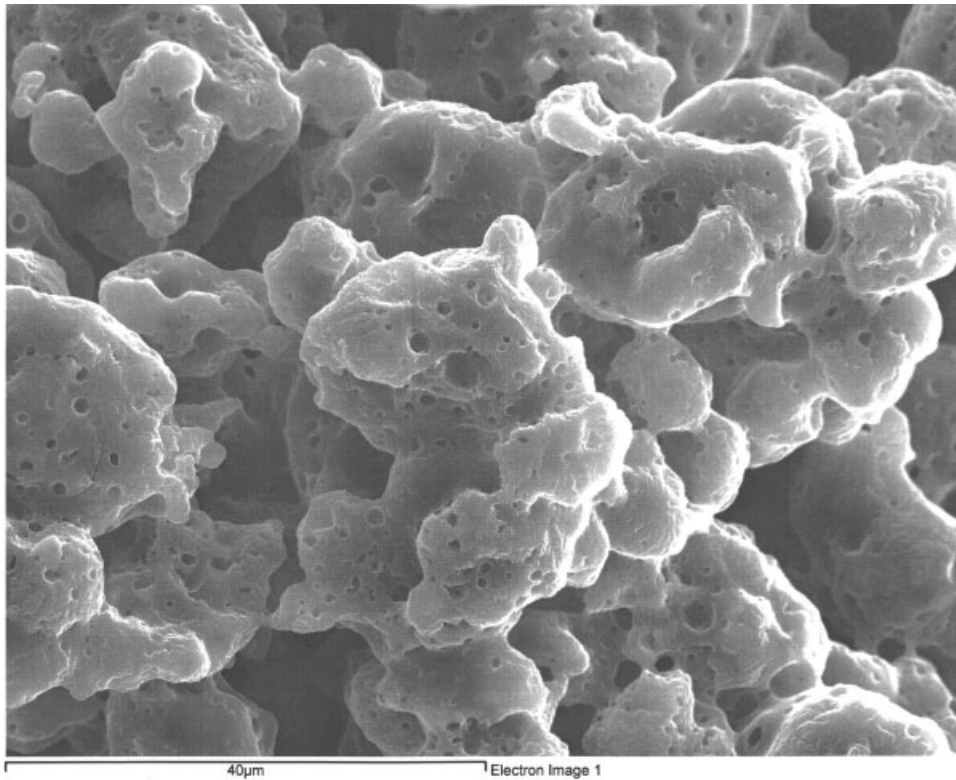


Figure 6 Seen under the sweeping electron microscope of anhydrous polymer.

polymer.¹³ The analysis of the results obtained by photoelectrons spectroscopy (Fig. 2) makes it possible to say that the sample is consisted of carbon, sodium, and oxygen, what is in agreement with the results obtained by EDX.

According to the results obtained starting from the spectra infrared, we can say that the polymer is consisted of macromolecular chains and each chain contains a significant number of acid functions. In aqueous medium, these acid functions dissociate and give rise to sites charged (COO^-). The repulsion of electrostatic nature between the same loads signs and the elasticity of the polymeric chains involves an expansion of the polymeric network, and consequently, a swelling of polymer to produce the gel. Indeed, if the number of dissociated acid functions is high (effect of the ionization level), the intensity of the elastic forces of repulsions is important.

The analysis of the diagram obtained by sweeping DSC under air (Fig. 4) shows that the polymer presents a first endothermic loss, which we can allot to eliminate water. The second loss, but exothermic, can be allotted to the degradation of the organic matter (combustion of the macromolecular chains). The color of polymer becomes maroon. A third loss, exothermic, can also be to assimilate to the degradation of the organic matter. The end product is of black color.

The analysis of the values of the heat capacities of polymer obtained by DSC, which are gathered in Table III, makes it possible to note that the value of the heat capacity varies with the nature of polymer. Indeed, it passes from 0.88 when the polymer is hydrated to 2.05 when this last becomes anhydrous.

The observation of the catches of sight obtained by electronic scan microscopy showed that after, the second loss, the pores start to appear on the surface of the sample. When the material is heated at higher temperatures (until 200°C) the surface becomes increasingly porous with also an increase in the size of the pores.

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