WATER SOLUBILITY OF COPPER SULPHATE FROM POLYMERS

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Abstract

To study the solubility of the copper sulphate in water, different types of tablets were prepared from different polymers with different percentages of $CuSO_4$. The tablets were left in water for some days and the amount of $CuSO_4$ released from the tablets was determined by measuring the absorbency of the final solution.

In the first phase of this work 10 samples were prepared, corresponding to two similar sets. The results from these two sets were not much different, and similar samples registered approximately the same amount of $CuSO_4$ in the water. By the seventh day more than the maximum amount of $CuSO_4$ expected was already registered in the solution, meaning that all the copper sulphate present had been transferred from the tablets to the water.

To try to get some more information about the influence of various factors on the solubility of the $CuSO_4$, another experiment was carried out and more tablets of different sizes and from different polymers were prepared.

From the results obtained it was possible to take some conclusions regarding the way both factors, thickness and type of polymer, influence the release of the copper sulphate from the tablets.

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Introduction

The kinetics of release of simple solutes into water, like sulphates incorporated in polymer matrices is of great importance, and has been subject to studies by many authors. Papadokostaki et all (1), for example, found out in his work that the kinetic of release obeyed a root t law, although there is an initial period where the diffusion coefficient increases with increasing solute load.

The process of solute diffusion, which is the major responsible for rate controlling, is dependent on the tortuosity of the available pathways (1).

The formation of a porous network in the matrix by mechanical rupture of the walls that separate the different holes that contain the solute particles, may influence the release rates of the solutes present (2).

One other mechanism is proposed by Papadokostaki et al (2) based on the combination of both interacting factors: solute release and water absorption-desorption processes. One other very important factor to consider when analysing the influence on the mechanism of solute release is the molecular relaxation processes that occur simultaneously.

Purdy et al (3) studied the interactions of solvent with copper in the diffusion and/or dissolution of copper into polymers, having concluded that copper dissolves easily in a wide variety of solvents, including water, under a pure oxygen atmosphere.

Shin et al (4) studied the release of certain chemicals from polymeric materials, having concluded that both pH and temperature controlled indirectly the release rate.

The release of different solutes may be governed either by osmotic pressure or by the diffusion process, not excluding the possibility of the influence of the matrix degradation at the final stage of the process. The rate of release may be determined by the polymer composition and molecular weight, coating thickness and device geometry (5).

Mi et al (6) prepared polymer tablets containing solutes by directly compressing the wet and dry blended powders containing the polymer and the solute, that were used to study the releasing rates.

Experimental

Materials:

- Tone P-300 Polymer (Union Carbide Chemical & Plastics SA)
- Tone P-700 Polymer (Union Carbide Chemical & Plastics SA)

- Tone P-767 Polyol HP (Union Carbide Chemical & Plastics SA)
- Capa 650 (Union Carbide Chemical & Plastics SA)
- Copper(II)-Sulphate-Pentahydrate: $CuSO_4.5H_2O$ (MERK)

Equipment:

- FONTIJNE TABLE PRESS TP 400
- PU 8620 UV/VIS/NIR Spectrophotometer PHILIPS

Experimental procedure

The experimental procedure to prepare the tablets was as follows:

a) Weight the quantities of polymer (Tone P-300) and $CuSO_4$ needed.

b) Melt the polymer (Tone P-300) in a glass by heating for 1-2 minutes.

c) Add the copper sulphate and mix the two.

d) Fill the holes of the mould[1] with the melted mixture.

e) Press during 1-2 minutes at 80ºC with 100 kN.

f) Take the tablets out of the mould.

g) Keep in a closed plastic bag.

The experimental procedure to measure the absorbency of the tablet solutions was:

a) Put three small (or one big) tablets into a container with 20.00 ml of distilled water.

b) Measure the absorbency of the solution.

The characteristics of the tablets produced according to the procedure described above and used in the first two sets of samples (set A and set B) are presented in tables 1 and 2.

Table 1 - Quantities used in the preparation of the tablets for sets A and B.

Tablet reference	$CuSO_4$ (g)	Polymer (g) *(Tone P-300)*	Total (g)	% of $CuSO_4$ (w/w)
T50	20.00	20.00	40.00	50.0
T30	10.90	25.00	35.90	30.4
T25	8.30	24.80	33.10	25.1
T20	6.00	24.00	30.00	20.0
T10	2.50	22.50	25.00	10.0

[1] The dimensions of the tablets made with this mould are: diameter = 10 mm, thickness = 2 mm.

Table 2 - Characteristics of the tablets for sets of samples A and B.

Tablet reference	Characteristics
T50	Not well pressed, with some bubbles of air. The colour is uniform, strong blue.
T30	Better pressed. Colour asymmetrically distributed, with some dark blue areas and some clear blue (or white) areas.
T25	Well pressed. Clear blue with some darker and clearer areas.
T20	Well pressed. Clear blue, more or less uniform, with some areas turning to brown.
T10	Well pressed. Clear blue with some asymmetries. Some brown areas.

Table 3 - Characteristics of the tablets for set C.

Polymer used	Notes on the preparation	Type	Notes on the tablets
P – 300	•Melted quickly. •Easy to mix both components. •Easy to put in the holes of the mould.	Thin	•Not well pressed. •Strong Blue with some white areas.
		Thick	•Well pressed. •Uniform strong blue.
P – 700	•Melted very slowly. •Very difficult to mix. •Very high viscosity. •Difficult to put in the mould.	Thin	•Well pressed. •Uniform clear blue.
		Thick	•Very well pressed. •Clear blue with some brown areas.
P – 767	•Melted very slowly. •Very high viscosity, almost like a ball of moulding clay or rubber. •Almost impossible to mix properly. •If heated after mixing, does not melt and becomes brown.	Thin	•Well pressed. •Clear blue with some brown areas.
		Thick	•Very well pressed. •Clear blue with some brown areas.
Capa 650	•Melted even more slowly. •Very high viscosity, almost like a ball of moulding clay or rubber. •Mixing is difficult. •If heated after mixing, it melts a little without degrading the polymer. Therefore it is easier to mould.	Thin	•Well pressed. •Uniform strong blue.
		Thick	•Very well pressed. •Strong blue with some light blue areas.

In the third set of samples (set C) all the tablets were prepared with 50% of $CuSO_4$ and 50% of Polymer (30.00 g of each), and two different types were made according to their size: Thin: diameter = 10 mm, thickness = 2 mm.

Thick: diameter = 10 mm, thickness = 10 mm.

The characteristics of the tablets used in set C are listed in table 3.

The experimental procedure to draw the calibration curve was as follows:

a) Prepare some standard solutions by weighting an exact amount of $CuSO_4$ and diluting it into a certain volume of distilled water.

b) Measure the absorbency of these solutions.

NOTES: - The absorbency of the water (Reference) was set to zero.

- The wave length of measurement was 810.

The characteristics of the samples used as standards to determine the calibration curve are presented in table 4.

Table 4- Preparation of the standards for drawing the calibration curve.

Standard nº	Amount of $CuSO_4$ (g) diluted in 25.00 ml	Concentration of $CuSO_4$ (g/l)
1	0.025	1.0
2	0.075	3.0
3	0.175	7.0
4	0.325	13.0
5	0.500	20.0
6	0.750	30.0

Results and discussion

Calibration curve

The calibration curve consists of a set of points that allow us to plot the absorbency of the solution versus the concentration of $CuSO_4$. Those points were determined by measuring the absorbency of a set of standard solutions, prepared according to the procedure described earlier, and whose characteristics are those in table 4.

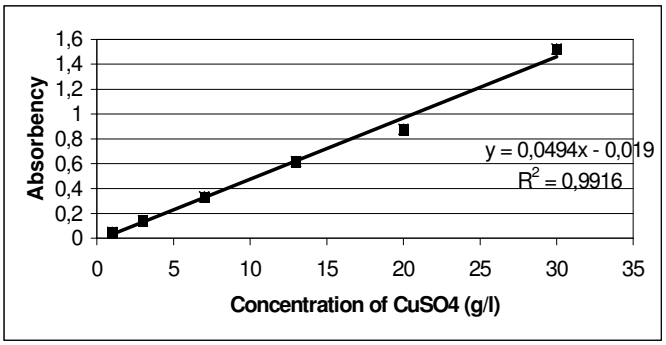
The measured absorbency of the standard solutions was registered along time in table 5, and it is possible to verify that after the first day the absorption of the standards

was maintained approximately constant. The data used to draw the calibration curve in figure 1 was naturally the data from the last day, that in this experiment corresponds to the 7th day.

Table 5 - Absorbency measurements of the standard solutions.

Standard	Absorbency				
nº	Day 0	Day 1	Day 2	Day 5	Day 7
1	0.039	0.054	0.051	0.051	0.049
2	0.161	0.143	0.145	0.141	0.141
3	0.301	0.337	0.335	0.333	0.333
4	0.492	0.618	0.627	0.615	0.617
5	0.739	0.872	0.876	0.869	0.876
6	1.014	1.512	1.520	1.523	1.522

Figure 1- Calibration curve.



The calibration curve was found to be approximately a straight line of the form:

abs = a + b * conc. (g/l) (1)

where b is the slope and a the absorption when the concentration is zero.

The experimental value of a should be as close to zero as possible for it was defined that the absorption of pure water was zero.

The values for a and b in equation (1) were found to be:

a = -0.019

b = 0.049 (l/g)

with a correlation coefficient of 0.9958.

Absorbency measurement of the tablet solutions

In the first part of this work 10 samples were prepared, consisting of two sets denominated by set A and set B, and their expected absorbency was determined theoretically from the calibration curve as a function of the maximum concentration of $CuSO_4$ that would be expected in the solutions. Those results are presented in table 6.

The maximum theoretical concentration of $CuSO_4$ in the sample's solutions was calculated assuming that the copper Sulphate was uniformly distributed through all the tablets. Therefore,

$$W(CuSO_4) = x(CuSO_4) * W(3 \text{ tablets}) \text{ (g)} \quad (2)$$

and

$$Conc(CuSO_4) = W(CuSO_4) * 1000/20 \text{ (g/l)} \quad (3)$$

where $\underline{x}$ represents the weight fraction and $\underline{W}$ the weight.

Table 6 – Expected absorbency of the samples used in sets A and B.

Sample nº	% of $CuSO_4$ (w/w)	Weight of 3 tablets (g)	Vol. Distilled water (ml)	Max. Conc. $CuSO_4$ (g/l)	Correspond. Absorbency (*)
Set A					
1	50.0	0.8435	20.00	21.0875	1.014
2	30.4	0.6879	20.00	10.4561	0.493
3	25.1	0.6345	20.00	7.9630	0.371
4	20.0	0.5858	20.00	5.8580	0.268
5	10.0	0.5495	20.00	2.7475	0.116
Set B					
6	50.0	0.8442	20.00	21.1050	1.015
7	30.4	0.6980	20.00	10.6096	0.501
8	25.1	0.6062	20.00	7.6078	0.354
9	20.0	0.5950	20.00	5.9500	0.273
10	10.0	0.5363	20.00	2.6815	0.112

(*) Calculated from the calibration curve: equation (1).

In figures 2 and 3 the absorbency of the samples in sets A and B is represented as a function of time.

Figure 2 – Absorbency measurements for set A of samples.

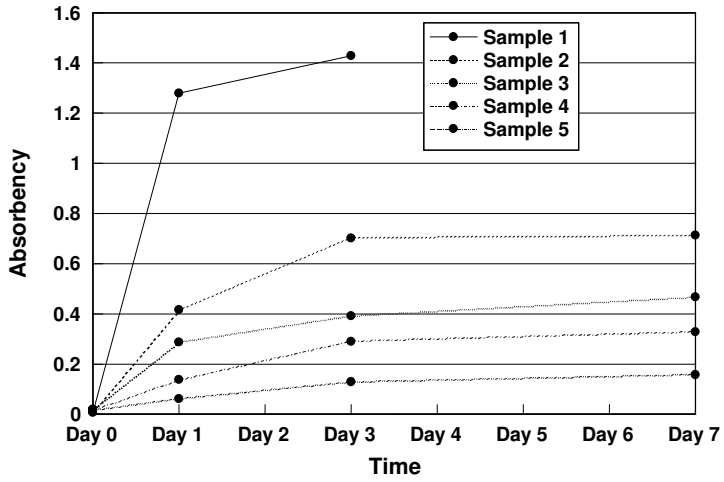
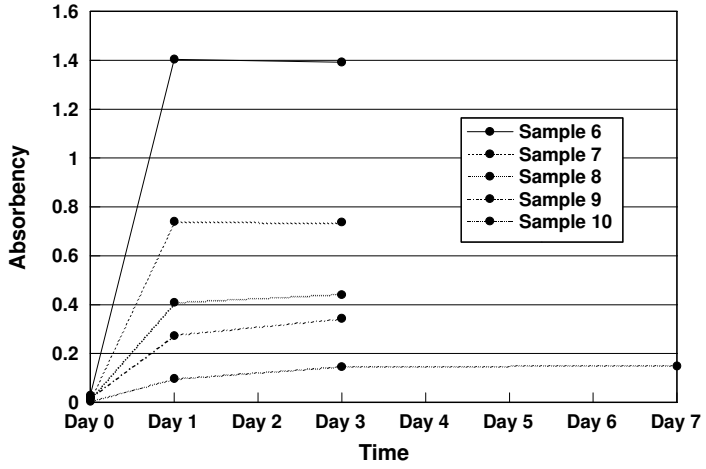


Figure 3 – Absorbency measurements for set B of samples.



The results from these two sets of samples are not much different and show that similar samples originated approximately the same amount of $CuSO_4$ in the water. In table 7 the relative percentage over the expected value of absorbency is presented.

Table 7 - Results from sets A and B of samples.

Sample nº	% over conc. $CuSO_4$ (*)	Day of confirmation
1 6	41 37	3 3
2 7	45 47	7 3
3 8	26 25	7 3
4 9	22 26	7 3
5 10	36 30	7 7

(*) Calculated relatively to the expected absorbency:

$$\% = \frac{\text{measured abs. - expected abs.}}{\text{expected abs.}} * 100$$

By the seventh day more than the maximum amount of $CuSO_4$ expected is already registered in the solution, meaning that all the copper sulphate present has been transferred from the tablets to the water.

The measurements made after the maximum concentration of $CuSO_4$ has been registered were made to confirm that fact and do not differ much from the previous ones. Therefore, by the 3rd day practically all the copper Sulphate had actually left the tablets.

During the first experiment it was possible to notice that for higher concentrations of $CuSO_4$ the tablets were not so consistent and would break easily when in water. This could be due to insufficient pressing while they were being prepared or to the high amount of $CuSO_4$ present.

To try to get some more information on the influence of these factors in the structure of the tablets some more tablets of two different sizes were prepared and more polymers were used. In table 8 the characteristics of these tablets are presented as well as the corresponding expected absorbency determined by the calibration curve.

According to the results of the first experiments, at least by the 7th day the transference of the copper sulphate from the tablets to the water has been completed. Therefore, the time scale-up of the measurements has been altered and more measurements were made in the first days.

Table 8 – Characteristics of the samples for set C.

Sample nº	Type of polymer	Type of tablet	Weight of tablets (g)	Max. conc. $CuSO_4$ (g/l)	Corresp. Absorb. (*)
11	P – 300	Thin	0.8009	20.0225	0.962
12	P – 300	Thin	0.7938	19.8450	0.953
13	P – 300	Thick	1.2823	32.0575	1.552
14	P – 300	Thick	1.2213	30.5325	1.477
15	P – 700	Thin	0.7553	18.8825	0.906
16	P – 700	Thin	0.7660	19.1500	0.919
17	P – 700	Thick	1.2265	30.6625	1.483
18	P – 700	Thick	1.1942	29.8550	1.444
19	P – 767	Thin	0.7465	18.6625	0.895
20	P – 767	Thin	0.7306	18.2650	0.876
21	P – 767	Thick	1.2187	30.4675	1.474
22	P – 767	Thick	1.2549	31.3725	1.518
23	Capa 650	Thin	0.8289	20.7450	0.998
24	Capa 650	Thin	0.8615	21.5375	1.036
25	Capa 650	Thick	1.2896	32.2400	1.561
26	Capa 650	Thick	1.2462	31.1550	1.508

(*) Calculated from calibration curve: equation (1).

In figures 4 and 5 the absorbency of the samples 11 to 26 is registered for a period of 24 days.

Figure 4 – Evolution with time of absorbency for samples 11 to 18.

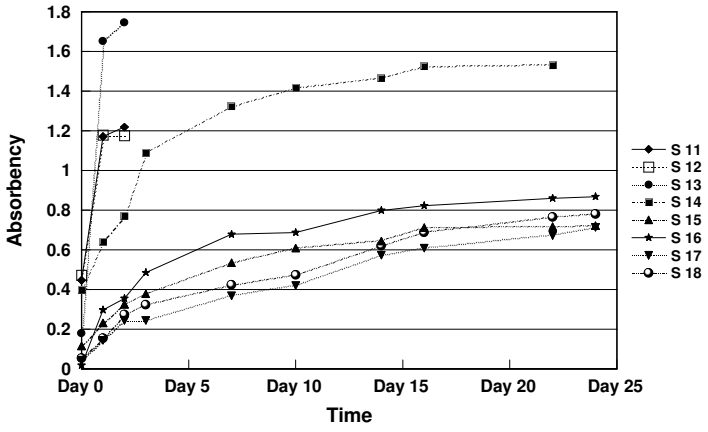


Figure 5 – Evolution with time of absorbency for samples 19 to 26.

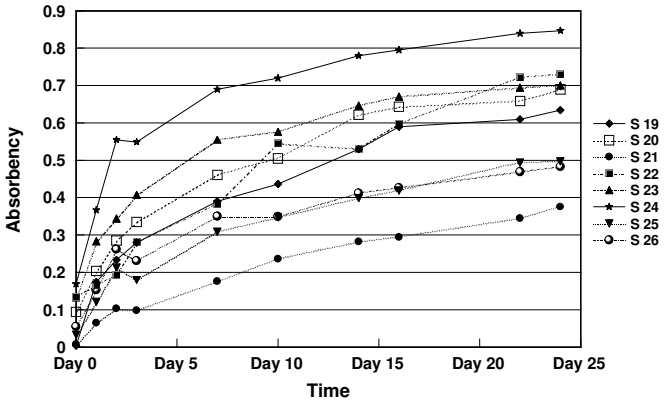


Table 9 – Results from the second experiment (set C of samples).

Polymer used	Type of tablet	Sample nº	% of solubility at last day (*)
P - 300	Thin	11	> 100
		12	> 100
	Thick	13	> 100
		14	> 100
P - 700	Thin	15	80
		16	94
	Thick	17	48
		18	54
P - 767	Thin	19	71
		20	79
	Thick	21	26
		22	48
Capa 650	Thin	23	70
		24	82
	Thick	25	32
		26	32

(*) Calculated relatively to maximum absorbency: % solubility = (abs. at last day) / (max. abs.) * 100 %

In table 9 the degree of solubility of the copper sulphate in water, according to type and shape of the tablets is shown, according to type and shape of the tablets. The degree of solubility was calculated as a percentage of absorbency relatively to maximum absorbency expected.

From the results presented, it is possible to infer that both factors, type of polymer and thickness of the tablet, influence the degree of solubility of the $CuSO_4$.

As could be expected, thicker tablets retain the $CuSO_4$ for longer time than the thinner ones. This behaviour is general and concerns all four types of polymers tested. In fact, table 9 shows that the percentage of solubility is always less for thicker tablets.

The type of polymer is also an important factor, and tablets made from P-300 released all the $CuSO_4$ quite easily (thin tablets on the 1st day and thick tablets on the 16th day). The polymers that seem to retain better the $CuSO_4$, and in a similar way, are P-767 and capa 650.

In table 10 is indicated the order by which the types of tablets release or would release all the $CuSO_4$ present.

Table 10 - Order of release of the $CuSO_4$.

Order of release	Type of tablet	
1	P-300	Thin
2	P-300	Thick
3	P-700	Thin
4	P-767	Thin
5	Capa 650	Thin
6	P-700	Thick
7	P-767	Thick
8	Capa 650	Thick

Conclusions

From this work is possible to conclude that the degree of solubility of copper sulphate is both influenced by the type of polymeric material used to produce the tablets and it's size.

As to the type of polymer, the behaviour of the polymers tested is different, which is easily understanding regarding their different macromolecules and consequently different structures.

Concerning the factor size, and as would be expected according to mass diffusion laws, thicker tablets retain the copper sulphate during more time than thin ones.

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