Pergamon

Cement and Concrete Research 31 (2001) 1539–1547

CEMENT AND CONCRETE RESEARCH

Characteristics of acrylic latex-modified and partially epoxy-impregnated gypsum

Adnan Çolak

Department of Civil Engineering, Faculty of Engineering, İstanbul University, 34850, Avcılar, İstanbul, Turkey

Received 6 February 2001; accepted 12 June 2001

Abstract

The properties of unmodified, acrylic latex-modified and partially epoxy-impregnated gypsum composites are investigated. A hyperbolic function of the form $ax/(1+bx)^n$ is derived empirically to describe the water/gypsum ratio dependence of the mechanical properties of gypsum. This function shows good agreement with the test results. The water/gypsum ratios, which give the maximum mechanical properties, are dependent on the material parameters n and b in proposed function, the values of which lie between 17.8% and 18.14%. The setting times of acrylic latex (methacrylic acid esters and styrene)-modified gypsum composites increase with an increase in latex content in the mix. These composites show a clear improvement in flexural strength. However, their compressive strengths remain almost in the same range of the unmodified gypsum. Epoxy impregnation does not lead to a significant increase in splitting tensile strength. The durability of the composites is examined by determining their behaviour in water after different periods. Seven days of immersion in 20°C water causes a reduction of about 70% in the mechanical strengths of latex-modified gypsum, whereas epoxy (diglycidyl ether of bisphenol A epoxy resin cured with an alkylenediamine curing agent)-impregnated gypsum composites with a surface coating of epoxy retain 100% of their original strengths even after 7 days exposure to water.

Keywords: Gypsum; Acrylic latex; Epoxy; Physical; Mechanical and durability

1. Introduction

Water-related deterioration is the principal source of difficulty with calcium sulfate-based materials as it is with most building materials. The protection of gypsum requires prevention against penetration of moisture to avoid progress of damage. A variety of methods that are capable of preventing and controlling the degradation of gypsum have been used. The techniques used in the first method include protection of gypsum by waterproofing materials. The method depends on the formation of a good bond between the gypsum and the protective polymer and is therefore prone to adhesion failure because of the critical surface preparation requirements. Waterproofing materials are applied on gypsum surface to form impervious coatings that prevent the passage of water in liquid form and may also retard vapour transmission in varying degrees, depending on the type of coating. Since the treatment prevents the ingress of water in liquid form, it also stops the transport of water-soluble salts into the gypsum. Various types of polymers are used for this purpose. In an application, the weatherability of gypsum is considerably improved by using a surface coating based on chlorosulfonated polyethylene [1]. In the second method, the ingress and migration of moisture in liquid and vapour can be prevented or retarded to varying degrees by the incorporation of a waterproofing admixture in gypsum mix. A waterproofing admixture is a powder, liquid or suspension, which, when mixed with fresh gypsum, imparts a water repelling or hydrophobic property to the hardened gypsum. The most widely used waterproofing admixtures for gypsum are metal stearates, siliconates, acrylics and methacrylates. In a study [2], high-strength gypsum products resistant to moisture are obtained by pressing the hemihydrate at low pressure in the presence of 0.2–2% Al stearate. A development [3] in which a water-soluble alkyl siliconate is added to the gypsum (at the rate of 0.1% on the weight of the calcium sulfate hemihydrate) produces casts with reduced

E-mail address: adnan@istanbul.edu.tr (A. Çolak).

PII: S0008-8846(01)00575-0

Table 1
Properties of acrylic latex

Type of latex	Methacrylic acid esters and styrene
Appearance	Milky white aqueous dispersion
Solid content (%)	30 ± 2
pH	9.5–10
Specific gravity at 20°C (g/cm^3)	1
Viscosity at 25° (mPa s)	11

water absorbency. The amount of additive could be raised to 1% or 2% for improvement in the performance. Bijen and Van Der Plas [4] form a moisture-resistant gypsum composite that contains a thermosetting acrylic polymer in dispersion state and high level of glass fiber (13% by weight). Even at high moisture contents up to 9%, the composite is still quite strong, with flexural strengths of approximately 35 MPa. However, one of the serious drawbacks in the use of water-soluble polymers is that these types of admixtures are effective in maintaining water repellency only if present in sufficiently high concentrations. Another effective means of protecting gypsum from moisture is to use water-insoluble or hardly soluble vinyl-type monomers such as Me-methacrylate [5]. The strength and durability of the hardened gypsum are improved considerably by this type of polymer. Some proprietary admixtures combine materials from two or more groups and may be regarded as multifunctional. The object of such composite mixtures is to impart waterproofing without strength loss. The studies indicate that gypsum products with good waterproofness are made by blending organic products with each other [6] or with organic resins such as urea–formaldehyde and lignin [7]. The latter formulation is design to deal with the problem of water penetration without affecting the strength.

Inorganic products are also used for waterproofing purposes. In this treatment, hardened gypsum products are immersed in an aqueous sodium carbonate [8] or barium sulfate [9] solution to form waterproof layers on the surface of gypsum.

In this study, two methods were applied to improve the resistance of gypsum to water. In the first method, the plaster was modified with acrylic latex. The latex/gypsum ratio was chosen as the quantitative parameter for investigating the improvement of resistance of gypsum to water by acrylic latex. In the second method, epoxy-impregnated gypsum specimens with a surface coating of epoxy were tested after different periods of immersion in water at 20°C. The effect of immersion in water on the water absorption and the mechanical strengths of the composites was investigated.

2. Experimental materials and methods

The specimens were prepared with the hydration of calcium sulfate hemihydrate, (β-hemihydrate). For the latex-modified gypsum, acrylic latex was used. The properties of the latex are given in Table 1. The latex/gypsum ratio was varied from 5% to 15% by weight of gypsum. The quantity of water was adjusted to achieve a 32 ± 2 mm constant indentation of the Vicat probe. In a second series of experiments, water was kept constant to eliminate the effect of the water/gypsum ratio on the results. The setting times of the acrylic latex-modified gypsum specimens were determined by Vicat needle. After the castings were made, they were cured in laboratory conditions at 20°C and 65% relative humidity (R.H.) for 7 days followed by drying in an oven at 40°C for 24 h. Porosities were measured by using water displacement method. Density was calculated from the mass and volume of the sample. Flexural strength was determined by using 4 × 4 × 16 cm specimens tested under three-point loading on a span on 10 cm. To determine compressive strength, 4 × 4 × 4 cm specimens were tested. For the epoxy-impregnated gypsum, two kinds of epoxy formulations were used. The properties of epoxy formulations are given in Table 2. The specimens used in this process were 20 mm diameter × 40 mm long gypsum cylinders. The water/gypsum ratio was varied between 50% and 100%. As soon as the gypsum specimens were set, they were stored in laboratory conditions for 24 h. Then, they were dried to constant weight at 40°C followed by cooling to room temperature in a desiccator. The specimens were impregnated with the EP1 and EP2 epoxy formulations for 30 and 60 min and then were polymerised at 20°C for 7 days. After polymerisation, the epoxy-impregnated gypsum specimens were not cleaned and had a surface coating of epoxy with a thickness ranging from approximately 0.5 mm up to 1 mm. Splitting tensile test was applied to the specimens. The depth of impregnation from surface was determined by visual examination of the cut sections of samples.

Table 2
Properties of epoxy formulations

Epoxy system	Resin	Reactive diluent	Hardener	Viscosity at 30°C (mPa s)
EP1	Diglycidyl ether of bisphenol A	Diglycidyl ether	Trimethylhexamethylenediamine	70
EP2	Diglycidyl ether of bisphenol A	Diglycidyl ether	Triethylenetetramine	130

Table 3
Physical and mechanical properties of gypsum

Water/gypsum (%)	Density (g/cm^3)	Setting time (min)	Theoretical flexural strength (MPa)	Theoretical compressive strength (MPa)
50	1.34	6	7.33	17.26
60	1.20	10	5.77	13.41
70	1.10	13	4.54	10.37
80	1.00	15	3.57	8.03
90	0.94	16	2.83	6.23
100	0.88	18	2.26	4.86

The durability of latex-modified and epoxy-impregnated gypsum composites was examined by determining its behaviour in water. The mechanical strengths and water absorption values of the composites immersed in water were determined at different time periods.

3. Results and discussion

3.1. The properties of gypsum

The test results of the unmodified specimens for which the water/gypsum ratio is varied between 50% and 100% are presented in Table 3. It is seen that the density and mechanical strengths of the gypsum decrease and the setting times increase as the water/gypsum ratio is increased. The change of mechanical strengths as a function of water/gypsum ratio consists of two parts, i.e., ascending and descending part. In the fist part, the mechanical properties of the gypsum increase up to water/gypsum ratio required for its complete hydration. In the second part, which begins from this ratio, the mechanical properties of the gypsum decrease as the water/gypsum ratio is increased. The mechanical behaviour in the descending part can be described by a mathematical function in the form of hyperbola [10]. The mechanical strengths of the gypsum specimens were calculated and presented in Fig. 1. The applicability of the test data obtained for the gypsum to the proposed function was investigated. The proposed equation is

$$y = ax/(1+bx)^n \tag{1}$$

where a, b and n are the material parameters to be determined and y and x are the mechanical properties of the gypsum and water/gypsum ratio, respectively.

Using Eq. (1), it is possible to predict both compressive and flexural strengths of the gypsum. However, several additional conditions have to be satisfied by Eq. (1) to predict an acceptable mechanical behaviour–water/gypsum ratio curve. These conditions are as follows:

At $x=0$, $y=0$
(y; represents mechanical properties of gypsum).
At $x=\infty$, $y=0$.

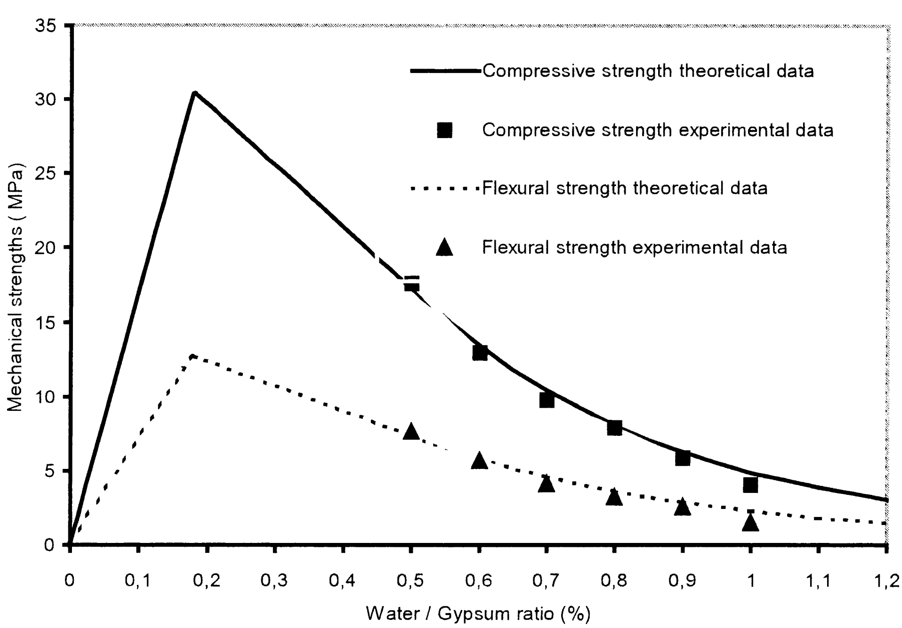

Fig. 1. Theoretical and experimental mechanical strengths of gypsum.

Table 4
Material constant, correlation coefficients and x_m values for gypsum

Mechanical properties	Material constant			Correlation coefficient (r^2)	x_m (%)
	a	b	n		
Flexural strength	213.396	1.067	6.263	.98	17.8
Compressive strength	489.782	0.84	7.564	.98	18.14

The proposed equation satisfies these boundary conditions.

$$\mathrm{d}y/\mathrm{d}x = 0, \quad x = x_m$$

where x_m is the water/gypsum ratio, which gives the maximum mechanical properties. By solving the latter condition, the following result is obtained for the value of x_m.

$$x_m = 1/b(n-1) \tag{2}$$

As seen in the Eq. (2), x_m is dependent on the material parameters n and b in the proposed equation. The nonlinear least-square method was used to calculate the material parameters in the proposed equation. The material parameters, correlation coefficients and x_m values found for gypsum are given in Table 4. The proposed equation proves satisfactory for defining the mechanical strengths of gypsum. As seen in Table 4, the correlation coefficients calculated by this equation approach one.

The water/gypsum ratios that give maximum mechanical strengths according to the Eq. (2) lie between 17.8% and 18.14%. The maximum flexural strength for the gypsum corresponds to the 17.8% water/gypsum ratio and the maximum compressive strength for the gypsum corresponds to the 18.14% water/gypsum ratio. These values are very close to the theoretical water value (18.3%) required for complete hydration of the calcium sulfate hemihydrate. The gypsum obtains its highest mechanical properties at a calculated value, which is very close to the theoretical water percentage necessary for its chemical reaction. The mechanical properties corresponding to the 18.3% water/gypsum ratio could not be determined since it is not possible to obtain a gypsum of pourable consistency using theoretical water quantity. However, it might be possible to produce a gypsum near to the theoretical water/gypsum ratio quantity considerably. The convenience of the mechanical properties determined in this case with the values calculated according to the proposed equation should be investigated.

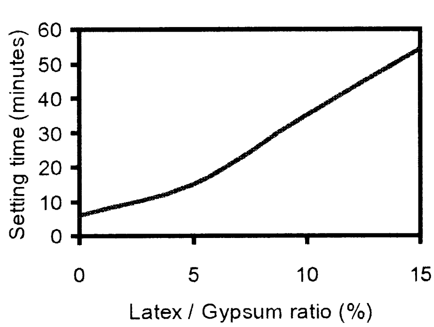

Fig. 2. The setting times of latex-modified gypsum with a constant water/gypsum ratio of 50%.

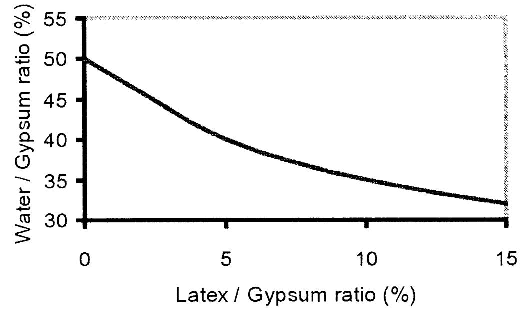

Fig. 3. Relation between water/gypsum ratio and latex/gypsum ratio at constant indentation (32 ± 2 mm).

3.2. Properties of acrylic latex-modified gypsum

The influence of the latex/gypsum ratio on the setting time of latex-modified gypsum specimens with a constant water/gypsum ratio of 50% is shown in Fig. 2. As can be seen in Fig. 2, the setting times of the composites change depending on the latex/gypsum ratio. In general, the latex interferes with the hydration of gypsum and causes prolonged setting times. This effect is more pronounced when the latex/gypsum ratio is increased. It can be seen that the addition of about 15% latex increases the setting time from approximately 6 to 54 min. Such a high extension of the setting time might be due to the interaction that occurs between the two systems.

Fig. 3 shows the water/gypsum ratio required to obtain latex-modified plaster with similar consistency as a function of the latex/gypsum ratio. For latex/gypsum ratio of 15%, a reduction of about 36% in water requirement is observed. The possibility of a significant reduction of the water/gypsum ratio by using acrylic latex appears to offer a potential for producing better gypsum plaster. The main advantage of the system is its good workability and ease of application when compared to other similar systems. However, these characteristic features of acrylic latex-modified gypsum paste are very much dependent on the admixture dosage rate. Small amounts of polymer in gypsum paste has little effect on workability. The addition of the polymer

Table 5
Test results for the latex-modified gypsum

Water/gypsum (%)	Latex/gypsum (%)	Density (g/cm^3)	Porosity (%)	Flexural strength (MPa)	Compressive strength (MPa)
50	0	1.35	31.3	8.8	16.9
50	5	1.27	30.6	9.0	16.2
40	0	1.53	25.9	10.8	24.4
40	5	1.41	24.9	10.7	25.0
40	10	1.36	22.0	11.7	20.3
35	10	1.41	19.4	12.6	24.6

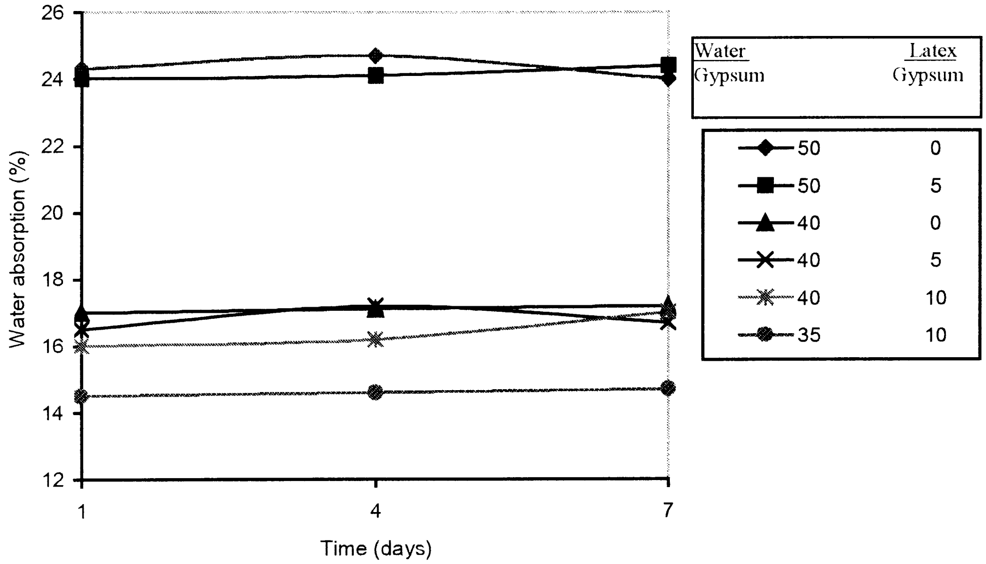

Fig. 4. Effect of water immersion on the water absorption of composites.

begins to have a significant effect when its content exceeds approximately 5%. Additions of the polymer between 5% and 10% by weight of gypsum dramatically reduce the water demand when compared to gypsum without acrylic latex. The decrease of water requirement may arise from the decrease in the quantity of gypsum and also from the lubricating effect of polymer particles in the latex. Higher proportions of the polymer usually between 10% and 15% by weight of gypsum modify further the properties of the mix. The results show that not only does the increase in the quantity of polymer strongly improve the workability of the fresh mix, but also it is capable of exerting a substantial influence on the flexural strength of the hardened composite.

The relationships between mechanical strengths and latex content at different water/gypsum ratios are given in Table 5. The flexural strength of latex-modified gypsum specimens with a water/gypsum ratio of 40% shows a minimum at 5% latex content. It subsequently increases with further increase in latex content to 10%. The water/gypsum ratio is kept constant for these specimens. Therefore, this parameter can not be regarded as the reason for

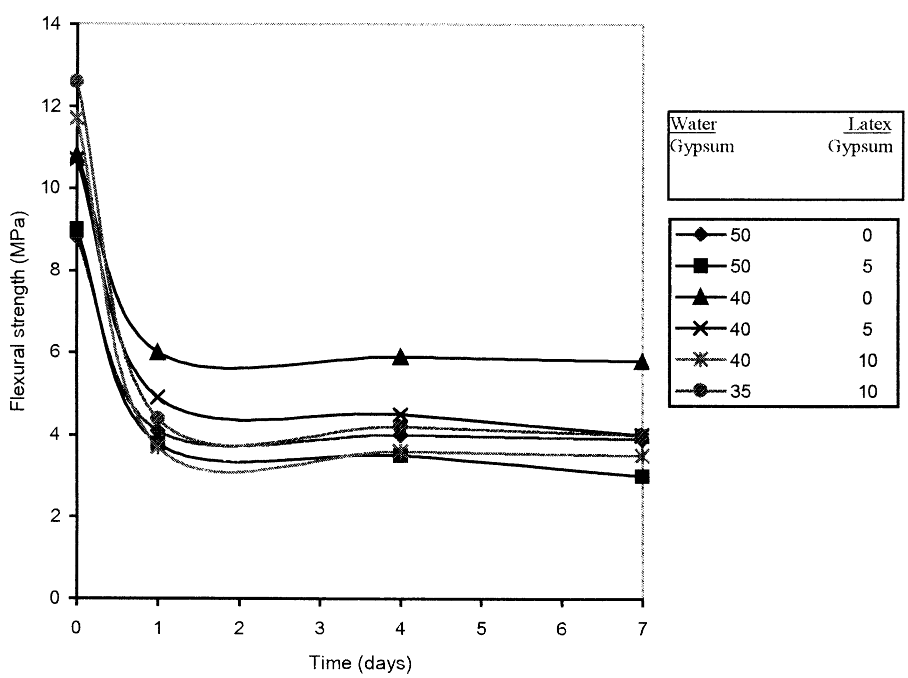

Fig. 5. Effect of water immersion on the flexural strength of composites.

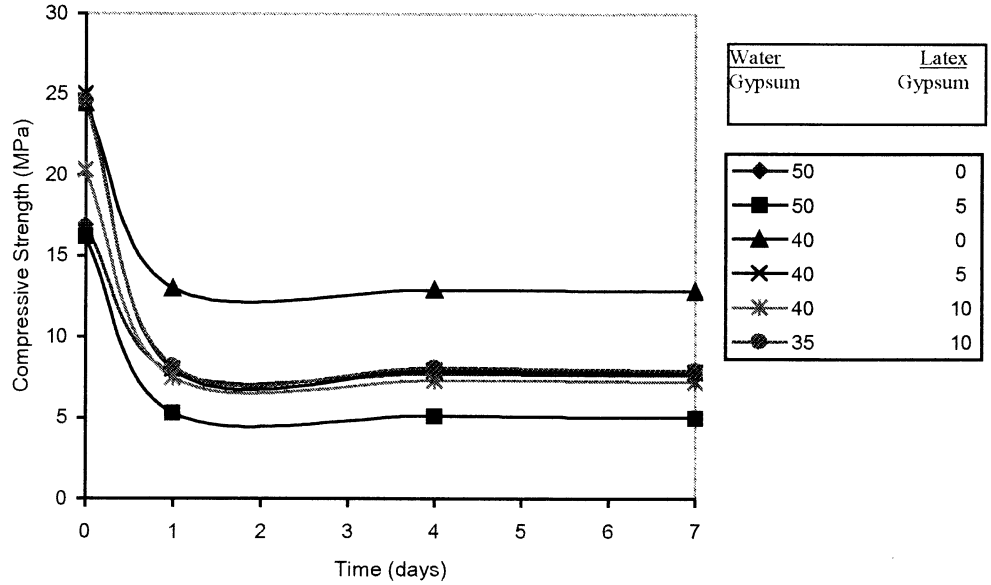

Fig. 6. Effect of water immersion on the compressive strength of composites.

strength improvement in the latex-modified gypsum [11]. The volume fraction porosities measured for the unmodified and modified gypsum specimens with a water/gypsum ratio of 40% are approximately constant with $0.22 \leq p \leq 0.26$ where p is the volume fraction of porosity. As a result, the increase in the flexural strength may be ascribed to the presence of latex in these samples and not to a reduction in porosities. However, it can be seen from Table 5 that the flexural strength of the composites increases with decreasing water/gypsum ratio and reaches a maximum value at 35% water/gypsum ratio. These findings clearly indicate that two mechanisms, i.e., the reduction in water content and the strengthening effect of the latex, will be responsible for the improvement of the strength of latex-modified gypsum [12].

The effect of latex addition on the compressive strength becomes remarkable at high latex/gypsum ratio. In considering the results obtained at constant water/gypsum ratios, it is found that latex-modified gypsum specimens with latex content of 5% have compressive values strength very close to unmodified ones. Latex addition of 10% causes a reduction of about 17% in compressive strength when compared with unmodified gypsum with a water/gypsum ratio of 40%. The decrease in strength is due to the high content of the soft polymeric material in the stiff gypsum matrix [13]. However, decreasing the water/gypsum ratio from 40% to 35% positively influences the compressive behaviour of latex-modified gypsum. The compressive strength of these specimens is quite close to that of unmodified gypsum with a water/gypsum ratio of 40%. Table 5 gives also the

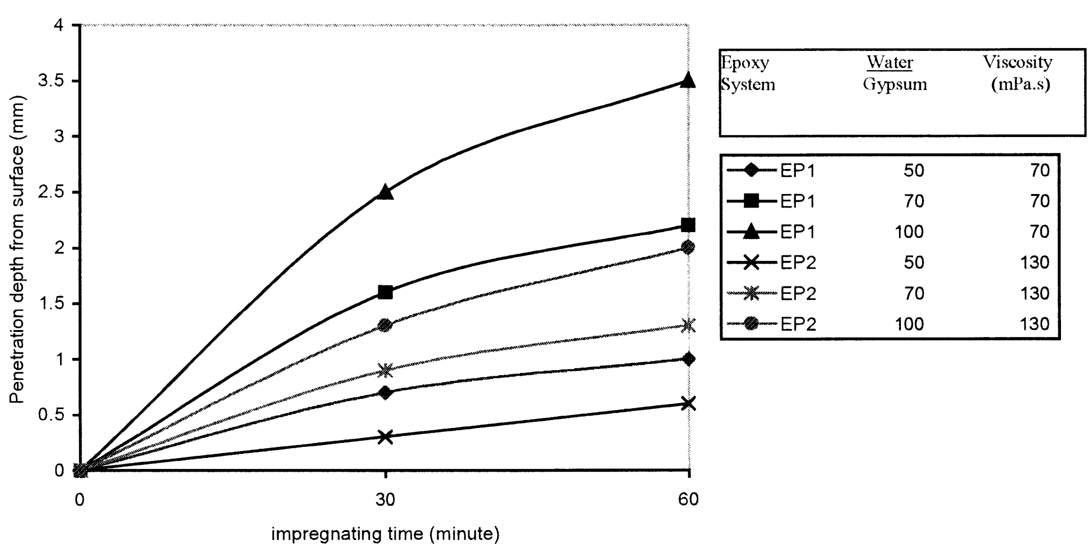

Fig. 7. Effect of gypsum quantity and viscosity of epoxy on penetration depth.

Table 6
Properties of epoxy-impregnated gypsum with a surface coating of epoxy

Epoxy system	Water/ gypsum (%)	Thickness of surface coating (mm)	Penetration depth from surface (mm)	Splitting tensile strength of impregnated gypsum (MPa)	Splitting tensile strength of unimpregnated gypsum (MPa)
EP1	50	0.5	1.0	4.68	4.63
EP1	70	1.0	2.2	3.00	2.93
EP1	100	0.7	3.5	2.11	1.68
EP2	50	0.6	0.6	4.65	
EP2	70	0.8	1.3	2.97	
EP2	100	1.0	2.0	1.72	

relationships between the density and the latex content. The decrease is due to air entrainment caused by the surfactant in the latex [14].

3.3. Effect of water on the properties of latex-modified gypsum

The effect of immersion in water on the water absorption and mechanical strengths of the latex-modified gypsum composites is shown in Figs. 4–6. The results obtained at constant water/gypsum ratios indicate that the water absorption values of the latex-modified gypsum composites are about the same as those of unmodified ones (see Fig. 4). It can be seen from Figs. 5 and 6 that the flexural and compressive strength of latex-modified gypsum are much lower than that of unmodified gypsum composite. The results show that after 7 days immersion in water, the unmodified gypsum with a water/gypsum ratio of 40% retains 50% of the original strength, whereas the latex-modified gypsum composites retains only 30% of the original strength. In general, immersion in 20°C water leads to rapid loss of flexural and compressive strength at all latex contents. This is due to potentially adverse effects of water on the polymer phase in latex-modified gypsum composite.

3.4. Properties of epoxy-impregnated gypsum

Fig. 7 shows the change of epoxy impregnation depth and rate with time. The curves are similar in shape, with the rate declining with increased penetration. The decrease in the rate of epoxy penetration into hardened gypsum may be the result of the viscosity of the impregnant to increase with time due to polymerisation [15]. It can be seen that the penetration depth and rate depend on the viscosity of epoxy and the gypsum quantity. The depth of epoxy penetration into hardened gypsum varies between 0.6 and 3.5 mm. Since the impregnated zone is only a small proportion of the cross-section of the sample, the tensile-splitting strengths of the epoxy-impregnated gypsum do not significantly increase compared to the unimpregnated gypsum specimens [16]. The experimental results in Table 6 show only a 25% increase in tensile-splitting strength at about 3.5 mm epoxy penetration depth.

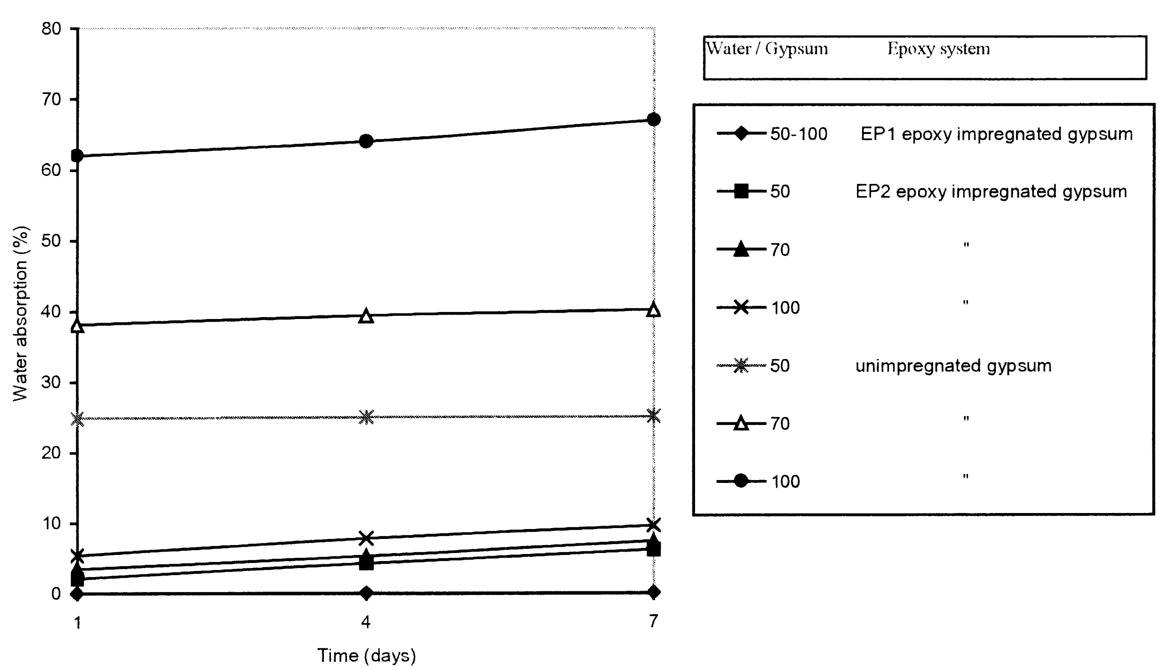

Fig. 8. Effect of water immersion on the water absorption of composites with epoxy impregnation.

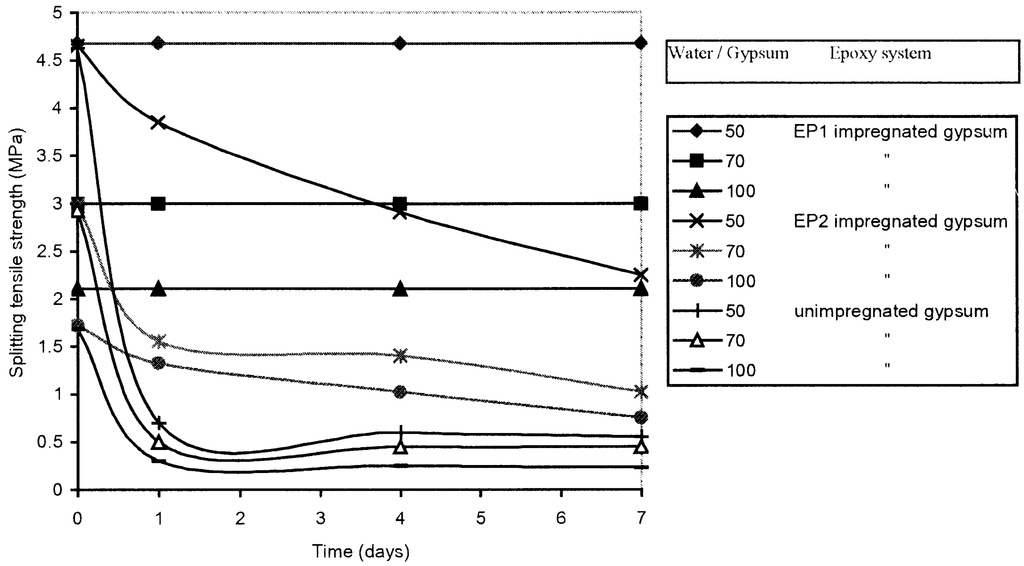

Fig. 9. Effect of water immersion on the splitting tensile strength of composites with epoxy impregnation.

3.5. *Effect of water on the properties of epoxy-impregnated gypsum*

Figs. 8 and 9 show the results of water absorptions and splitting tensile strength of unimpregnated and epoxy-impregnated gypsum after different periods of immersion in 20°C water. EP1 epoxy-impregnated gypsum composites show water absorption values approximately equal to zero. No change in splitting tensile strength of the composite with time could be detected. The results show that after 7 days of immersion in water, the composites retain 100% of their original strengths. These findings clearly indicate that EP1 epoxy formualtion forms on the gypsum a continuous and resistant protective layer, which, at least for 7 days, prevents the penetration of water. The increase in epoxy coating thickness from 0.5 to 1 mm does not influence the shielding function of EP1 epoxy formulation against the diffusion of water. EP2 epoxy formulation seems to act in a different manner; it is effective in reducing the speed of water entry but does not provide a water-tight barrier. Mechanical damage occurs with the ingress of water into gypsum.

The unimpregnated gypsum shows water absorption values higher than 67%. After 7 days of immersion in water, their tensile-splitting strengths decrease, with approximately 15% original strength being retained at all water/gypsum ratios.

4. Conclusions

The following conclusions can be drawn from this experimental investigation:

1. The acrylic latex in the form of a water-based suspension at high dosages tends to retard the hydration process. The effects show mainly as increased setting times.

2. The addition of acrylic latex to gypsum allows a remarkable reduction in the water/gypsum ratio.

3. The water absorption values of the latex-modified gypsum composites are about the same as those of unmodified ones. However, the water absorption of the composites is decreased with a reduction in water/gypsum ratio.

4. About 5% latex addition does not lead to increase in flexural strength compared to unmodified gypsum. However, increase in polymer content from 5% to 10% causes a significant improvements in flexural behaviour. Decreasing the water content from 40% to 35% positively influences the mechanical behaviour of latex-modified gypsum and leads to 43% increase in flexural strength compared to unmodified gypsum with a water/gypsum ratio of 50%.

5. The depths of penetration of EP1 and EP2 systems epoxy resins into the gypsum are found to vary between 0.6 and 3.5 mm. The increase in viscosity of epoxy resin during the first 30 min does not support a good penetration behaviour.

6. Epoxy impregnation does not lead to a significant increase in tensile-splitting strength.

7. EP1 epoxy-impregnated gypsum composites show water absorption values approximately equal to zero at the end of 7 days of water immersion, whereas the water absorption of the EP2 epoxy-impregnated gypsum composites tends to increase in time because of the slow ingress of water into gypsum.

8. Immersion in 20°C water does not influence the durability performance of the EP1 epoxy-impregnated gypsum with a surface coating of epoxy. After 7 days of immersion in water, the composites retain 100% of the original strength. The protection offered by EP1 epoxy system may be lost after a long-term period of water immersion. A potential solution to this problem is the evaluation of the product for a long-term period under natural aging conditions. However, the length of testing time may not be

satisfactory for obtaining the data that permit the prospective service life of the product to be determined with a high degree of accuracy. EP2 epoxy formulation does not prevent the mechanical damage caused by water since it is not effective in stopping the diffusion of water inwards into gypsum from the surface.

9. The proposed hyperbolic equation yields satisfactory results for the gypsum. Using this equation, the flexural and compressive strengths of gypsum can be predicted from its composition. The predictions compare very well with the experimental data.

References

[1] G.A. King, Symposium on New Building Materials and Components, Iraq, Oct., 1979.
[2] M. Deleuil, Gypsum construction parts, Chem. Abstr. 91 (1979) 145114d.
[3] E. Hofmann, M.J. Ridge, Australian Patent 249423, 1960.
[4] J. Bijen, C. Van Der Plas, Polymer-modified glass fibre reinforced gypsum, Mater. Struct. 25 (1992) 107.
[5] S. Murayama, A. Toko, High-strength gypsum products with good waterproofness, Chem. Abstr. 84 (1976) 78793q.
[6] S.W. Maier, A.J.H. Lamprecht, Gypsum product, Chem. Abstr. 90 (1979) 75711z.
[7] S.S. Zhavrid, A.K. Kalechits, P.P. Shashkel, T.P. Anikienko, Gypsum–polymer concrete mixture, Chem. Abstr. 90 (1979) 75708d.
[8] K. Matsuoka, T. Matsushita, Improving waterproofness of hardened gypsum products with sodium carbonate, Chem. Abstr. 84 (1976) 78811u.
[9] K. Matsuoka, T. Matsushita, Improving waterproofness of hardened gypsum products with barium sulphate, Chem. Abstr. 84 (1976) 78812v.
[10] A. Çolak, Estimation of mechanical properties of plaster depending on water/plaster ratio, Chim. Acta Turc. 24 (1996) 161–164.
[11] Y.-W. Mai, B. Cotterell, Porosity and mechanical properties of epoxy-resin modified cement mortar, Cem. Concr. Res. 16 (1986) 646–652.
[12] G. Zappia, F. Sandrolini, A. Motori, Premix PCC materials: Mechanical properties as a function of technological factors, Mater. Struct. 23 (1990) 436–441.
[13] L.M. Saija, Waterproofing of Portland cement mortars with a specially designed polyacrylic latex, Cem. Concr. Res. 25 (1995) 503–509.
[14] Y. Ohama, Polymer-Modified Mortars and Concretes, Concrete Admixture Handbook: Properties Science and Technology, Noyes Publications, Park Ridge, 1984, pp. 337–429.
[15] G.R. Moore, D.E. Kline, P.D. Cady, R.E. Weyers, P.R. Blankenhorn, Impregnation of concrete with hot epoxy resins, Cem. Concr. Res. 13 (1983) 721–727.
[16] ACI Committee 548, Guide for the use of polymers in concrete, ACI J. 83 (5) (1986) 798–829.