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Effect of Self Stress on Flexural Strength of Gypsum-Polymer Composites

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Self stress generated in polymer impregnated gypsum (referred as GPC) when it is composed is estimated, and its influence on flexural strength is discussed. The estimation of the self stress is based on measured values of shrinkage caused by polymerization of impregnated monomer and elastic modulus of dried gypsum base just before impregnation. The effect of this self stress on flexural strength of GPC is investigated. It was found that the following equation is valid to predict flexural strength of GPC (σ_b) in terms of the self stress as a variable: $\sigma_b = \sigma_{gb} + V_p(\sigma_p - \sigma_{sp})$, where σ_{gb} = flexural strength of gypsum base, V_p = specific volume of polymer, σ_p = tensile strength of polymer, and σ_{sp} = self stress generated in polymer phase. If extremely low water-gypsum ratio is adopted to prepare gypsum base, cracking is observed just after polymerization preceding any flexural loading. For somewhat higher water-gypsum ratio, specimens are not cracked, but their flexural strength is decreased after polymer impregnation. The self stress corresponding to this case turns out to be higher than the tensile strength of polymethyl methacryrate used for the impregnation. Since prediction of σ_{sp} in the equation is based on tri-axial compressive strain of gypsum base that is within its elastic region, σ_{sp} in polymer phase should positively exist. Even for this condition, the validity of the equation seems to be maintained, although the value in the parenthesis of the equation becomes negative. Based on this fact, an unstable physical state where one phase of a composite material is stressed beyond its macroscopic strength as an individual material owing to the crack arresting effect of the other phase (gypsum in this case) has been postulated. This state is designated as a "super-stressed" state, taking its resemblance with supercooling or supersaturation into consideration. ADVANCED CEMENT BASED MATERIALS 1998, 7, 1–7. *© 1998 Elsevier Science Ltd.*

KEY WORDS: Polymer impregnated gypsum, Flexural strength, Self stress, Composite law, Super stress

Polymer impregnated gypsum or gypsum-polymer composite (GPC) is manufactured by impregnating gypsum base with monomer and polymerizing it in situ by thermal-catalytic reaction, where drying of base material, evacuation of impregnation vessel, and impregnation of monomer are required prior to polymerization. A new type of material that exhibits high strength and high impermeability can be produced [1].

To reduce the total cost of the product, optimization of base material with reference to facility of processing, polymer content, and performance of the product is required.

For these purposes, optimization of porosity of gypsum base was experimentally conducted. Through this investigation, a seemingly contradicting fact that flexural strength is decreased after impregnation of polymer for positive polymer loading was found.

An analysis of this phenomenon is presented in this article together with a proposal of a crack propagation model and a composite law based on this model.

Preparation of Sample

Four gypsum bases having different porosities were prepared using three types of gypsum α and β as shown in Table 1. These bases were dried in a draft type of oven at 48°C for 5 days for gypsums A, B, and D, and for 3 days for gypsum C. These bases were placed in a container evacuated down to 800–933 Pa for 30 minutes. Then, methyl methacrylate (MMA) monomer mixed with 0.5% azobisisobutyronitrile was introduced to the container for impregnation. After 1 hour of impregnation, impregnated polymer was polymerized for 20 hours at 60°C in a heat medium that could minimize monomer loss from the bases.

Measurement Methods

Flexural strength and compressive strength were measured by a method prescribed as JIS R 5201 for beam

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TABLE 1. Properties of gypsum

Type of gypsum base	A	B	C	D
Type of gypsum	α	α	β	α
Raw material	Chemical	Natural	Natural	Chemical
Mixing water (%)	30	39	60	20
Specific gravity at demolding	1.95	1.86	1.64	
Specific gravity after drying	1.769	1.583	1.207	Mixed
Initial set (min)	6	30	15	with hot
Final set (min)	35	39	43	water of
Expansion (after 1 hour) (%)	0.236	0.016	0.126	70°C
Final expansion (%)	0.328	0.016	0.126	
pH of gypsum paste	7 ~ 8	11 ~ 11.5	5 ~ 6	
V_a	0.246	0.319	0.478	0.174
V_g	0.754	0.681	0.522	0.826
V_P	0.180	0.242	0.363	0.123

Note: V_a = specific volume of void; V_g = specific volume of gypsum.

specimens having dimensions 40 × 40 × 160 mm. Modulus of elasticity and Poisson's ratio were measured by a method prescribed in ASTM C469 for 50Φ × 100 mm cylindrical specimens attached with an electric strain gauge 20 mm in length. These tests were performed 3 days after polymerization.

Shrinkage due to polymerization was measured by a method prescribed as ASTM C 490-65 T for beam specimens having dimensions 25 × 25 × 280 mm. In this test, the original length was measured just before impregnation, and the shrinkage was determined for the length just after impregnation when the specimens were cooled down to 20°C.

Results of Measurements

In Table 2, the theoretical monomer loading is compared to the observed monomer loading. Theoretical porosity in this table is calculated from the specific gravity of dried gypsum (apparent) and that of dehydrate (assumed to be 2.32). To get the theoretical polymer loading, all voids are assumed to be filled with monomer of specific gravity 0.959. It is understood that the measured polymer loading is very close to the theoretical one.

Strength and elastic modulus of dried gypsum are shown in Tables 3 and 4.

Strength of GPC is shown in Table 5, and shrinkage of gypsum base due to polymerization of impregnated monomer is shown in Table 6.

From these values, it can be seen that flexural strength of gypsum A is decreased after impregnation, although compressive strength is significantly increased for every gypsum base after impregnation.

To determine a composite law existing in between these measurements, estimation of self stress was attempted.

Estimation of Self Stress

Shrinkage due to polymerization (Sp) is considered to be tri-axial in nature, and gypsum base is presumed to be compressed tri-axially up to this strain. Thus, self stress working in gypsum phase can be calculated from this strain and modulus of elasticity of gypsum base [2, 3].

Using bulk modulus of elasticity (K) and volumetric strain (ϵ_V), the macroscopic self stress (σ_{sg}) is written as:

$$\sigma_{sg} = K\epsilon_V \tag{1}$$

while (K) and (ϵ_V) are expressed by modulus of elasticity (E) and Poisson's ratio (μ) of gypsum base, respectively, as:

TABLE 2. Comparison of polymer loading

Type of Gypsum Base	Specific Gravity of Gypsum (dry)	Theoretical Porosity (%)	Theoretical Monomer Loading (%)	Measured Monomer Loading (%)
A	1.750	24.57	13.46	13.57
B	1.582	31.81	19.28	19.50
C	1.202	48.19	38.44	38.87

TABLE 3. Strength of dried gypsum

Type of Gypsum Base	Flexural Strength σ_{gb} (MPa)	Compressive Strength σ_{gc} (MPa)	
	15.9	43.4	52.3
A	16.9	53.9	44.0
	13.6	47.6	49.9
	14.7	63.8	62.1
Average	15.8	52.3	
	8.57	18.7	28.5
B	9.08	28.0	24.0
	7.65	26.2	28.2
	8.16	24.4	35.1
Average	8.37	26.6	
	5.31	17.2	16.6
C	5.00	20.5	16.1
	5.00	19.4	18.7
	7.04	17.2	19.2
Average	5.59	18.2	

TABLE 5. Strength of GPC

Type of Gypsum Base	Flexural Strength σ_{gb} (MPa)	Compressive Strength σ_{gc} (MPa)	
	10.6	126.3	—
A	10.4	123.1	116.1
	13.1	118.0	120.5
	10.9	111.6	107.8
Average	11.3	117.7	
	13.9	119.0	112.6
B	14.7	114.8	96.0
	12.3	116.1	105.2
	14.1	116.1	116.4
Average	13.8	111.9	
	15.4	81.0	86.1
C	11.7	91.0	91.6
	14.7	87.0	80.7
	15.4	81.0	84.2
Average	14.3	84.7	

$$K = \frac{E}{3(1 - 2\mu)}, \ \epsilon_V = 3Sp. \qquad (2)$$

Substituting eq 2 into eq 1:

$$\sigma_{sg} = E \cdot Sp/(1 - 2\mu). \qquad (3)$$

This compressive self stress should be balanced with tensile self stress (σ_{sp}) working in polymer phase that has cross-section (Vp) in a unit area of gypsum base. Then:

$$\sigma_{sg} + Vp\sigma_{sp} = 0. \qquad (4)$$

Since the strength measurement is performed about 3 days after the time of shrinkage measurement, effect of relaxation corresponding to this time difference should be taken into account.

The relaxation coefficient (η) should be multiplied by the self stress to obtain the true self stress working at the time of testing. The relaxation ratio for gypsum base for 0.8 stress ratio was found to be 8%, and relaxation ratio of polymer phase is assumed to be 40% from the literature. Then the total effect can be estimated as 0.92×0.60, that is, 0.55. $(1 - 2\mu)$ calculated from Table 3 is 0.53 on average for the three types of gypsum base. $\eta/(1 - 2\mu)$ is assumed to be unity in the following analysis for all cases. Springback due to this relaxation might explain negative creep of PIC, a strange phenomenon that has been reported by Steinberg et al. [4,5].

TABLE 4. Elastic moduli of dried gypsum

Type of Gypsum Base	Modulus of Elasticity $E \times 10^4$ (MPa)	Poisson's Ratio μ
	2.09	0.256
A	1.97	0.250
	1.89	0.215
Average	1.98	0.240
	1.31	0.238
B	1.36	0.228
	1.10	0.244
Average	1.26	0.237
	0.82	0.222
C	0.87	0.228
	0.77	0.215
Average	0.82	0.222

TABLE 6. Shrinkage due to polymerization

Type of Gypsum Base	Shrinkage Due to Polymerization Sp (%)		
	0.092	0.095	0.091
A	0.091	0.089	0.088
	0.096	0.088	—
Average		0.0912	
	0.083	0.088	0.090
B	0.086	0.082	0.088
	0.090	0.087	0.093
Average		0.0874	
	0.180	0.197	0.179
C	0.195	0.164	0.199
	0.187	0.204	—
Average		0.188	

TABLE 7. Self stress in gypsum (σ_{sg}) and polymer phase (σ_{sp})

Type of Gypsum Base	A	B	C
S_P	−0.000912	−0.000874	−0.001880
E (MPa) × 10^4	1.98	1.26	0.82
V_P	0.180	0.242	0.363
σ_{sg}	−18.05	−10.97	−15.35
σ_{sp} (MPa)	100.3	45.33	42.28

Therefore:

$$\sigma_{sg} = E \cdot Sp \tag{5}$$

$$\sigma_{sp} = -E \cdot Sp/Vp. \tag{6}$$

Using these equations, self stresses are estimated as shown in Table 7. Tensile self stress working in the polymer phase of GPC for the A type gypsum base is calculated as higher than the tensile strength of PMMA (68.4 MPa). In this case, the compressive strain of gypsum A 912 × 10^{-6} is far below its uni-axial elastic limit 2500 × 10^{-6}. Thus, the tensile stress should exist if eq 4 holds.

Estimation of Flexural Strength of GPC as a Function of Self Stress

Since polymer is formed in a continuous phase in a part of void that is originally created in gypsum base and microscopically incorporated with gypsum, the series model shown in Figure 1 can be applied for flexural strength where failure is initiated locally at the outermost skin of the specimen.

As the first approximation, the flexural strength of GPC is obtained by adding the contribution of polymer strength to the flexural strength of gypsum base:

$$\sigma_b = \sigma_{gb} + Vp\sigma_p. \tag{7}$$

An equation such as this, however, cannot be applied to a two-phase composite material where rupture in either phase leads to failure of the total system (c.f. tensile strain capacity of polymer is 10 or more times greater than that of gypsum).

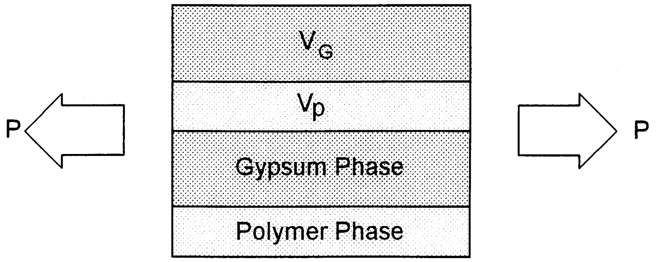

FIGURE 1. Series model.

In general, force is transmitted from one phase to another due to bond, friction, or mechanical intertwining. Local rupture of one phase does not necessarily lead to final failure of a composite material. In the case where the propagation path of the catastrophic crack rarely coincides with cracks pre-existing in one phase, eq 7 might hold in Griffith's theory even if the strain capacity of the two phases differs greatly, and the difference is compensated with microcracks that should develop locally before final rupture.

Since experimental data have not proved eq 7, the effect of self stress is introduced as:

$$\sigma_b = \sigma_{gb} - \sigma_{sg} + Vp(\sigma_p - \sigma_{sp}). \tag{8}$$

However, self stresses in this equation cancel each other, and eq 8 reduces to eq 7. Then, a new model for crack propagation is conceived as shown in Figure 2, where influence of microcracks that should develop in gypsum phase before rupture of polymer phase is taken into account. Accordingly, the self stress should be released locally on initial microcracking at the cracked ends of gypsum phase, and the stress variation due to the subsequent elastic springback is restrained gradually by bond or friction acting between two phases to give the stress distribution shown in Figure 2. Self stress in polymer phase also changes corresponding to this situation.

In accordance with the principle that the catastrophic crack should propagate through a path so that the minimum energy barrier is required, the catastrophic crack should be initiated in the maximum self stress region of polymer phase and should propagate through the minimum self stress region of the gypsum phase. In an extreme case, the catastrophic crack might selectively propagate along pre-cracked points of gypsum phase. Distribution of the initial microcracks in gypsum phase and their relative size and location in comparison with the nucleus of the catastrophic crack might probably determine which is really the case. Here, it should be kept in mind that location of the maximum self stress region of polymer phase is furthest from the location of the initial microcracks.

If the former is the case, then:

$$\sigma_b = \sigma_{gb} + Vp(\sigma_p - \sigma_{sp}) \tag{9}$$

or substituting eq 6 into eq 9:

$$\sigma_b = \sigma_{gb} + Vp\sigma_p - ES_p \tag{10}$$

could be applied.

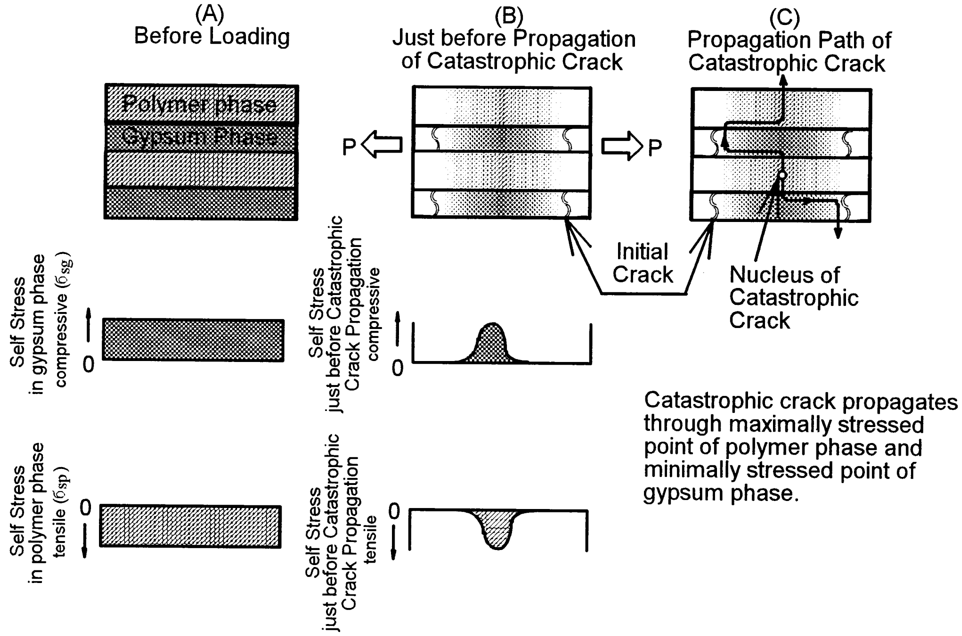

FIGURE 2. Transition of self stress and propagation path of catastrophic crack.

For an extreme case such as the latter one:

$$\sigma_b = Vp(\sigma_p - \sigma_{sp}) \tag{11}$$

might be supported.

Using these equations, estimation of flexural strength of GPC is performed as shown in Table 8.

Investigation into Flexural Strength

Observed values of flexural strength of GPC are compared to the values estimated by eqs 9 and 11 in Figure 3. It is clearly shown that eq 9 provides good prediction.

Experimental data are explained by eq 9 rather than eq 11. This strongly suggests that the initial microcracks that should develop in gypsum phase are three-dimensionally distributed in a discontinuous manner and are rarely hit upon by the catastrophic crack.

On the basis of the model shown in Figure 2 and Griffith's theory, it is natural that gypsum phase, which is fragmentarily sustained in continuous polymer phase, is as resistant as the original gypsum base against propagation of the catastrophic crack, if the pre-described situation is really the case.

TABLE 8. Theoretical prediction of flexural strength of GPC

Items	Type of Gypsum Base A	B	C	Unit	Remarks
σ_{gb}	15.8	8.37	5.59	MPa	
V_p	0.180	0.242	0.363	—	
$\sigma_p - \sigma_{sp}$	−31.9	23.0	26.1	MPa	
$V_p(\sigma_p - \sigma_{sp})$	−5.74	5.57	9.47	MPa	Eq 11
$\sigma_{gb} + V_p(\sigma_p - \sigma_{sp})$	10.06	13.94	14.97	MPa	Eq 9
Observed σ_b	11.3	13.8	14.3	MPa	

The term ($\sigma_{gb} - \sigma_{sg}$) in eq 8 could be regarded as flexural strength of gypsum that is pre-stressed by the shrinkage of polymer. The observed flexural strength of GPC is much smaller than this value. The main reason may be explained by the fracture model shown in Figure 2. It should be noted that self stress that is generated microscopically in a composite material is fundamentally different from pre-stress that is macroscopically introduced in a structural member.

Superstressed State

Flexural strength of GPC is decreased after impregnation for type A gypsum. This is quite strange, because

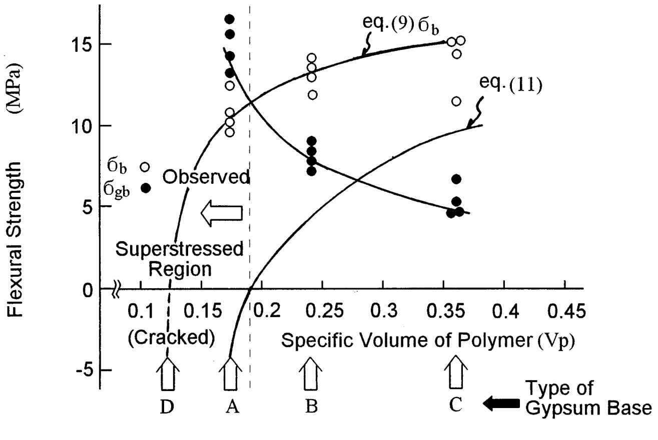

FIGURE 3. Flexural strength and specific volume of polymer.

original void space that makes no contribution to strength is filled with polymer that has tensile strength much higher than that of gypsum.

As shown in Table 3, self stress in polymer phase is higher than the tensile strength of polymer for this gypsum, and the term ($\sigma_p - \sigma_{sp}$) in eq 9 is calculated as negative. By assuming apparent contribution of polymer strength to be negative, the amount of strength decrease is also predicted for this case by eq 9 as shown in Table 8 and Figure 3. Self stress in gypsum phase (σ_{sg}) corresponding to this σ_{sp} is within the elastic limit and is positively working. Therefore, this self stress in polymer phase should also exist. Thus, an unstable physical state where one phase of a composite material is stressed beyond its macroscopic strength owing to the crack arresting effect of the other phase is postulated. This state is termed the "superstressed state."

Effect of Self Stress on Compressive Strength of GPC

As described previously, dried gypsum base is tri-axially compressed by shrinkage of the impregnated polymer. Generally, it is well known that the uni-axial compressive strength (σ_1) of a material is increased by lateral pressure ($\sigma_2 = \sigma_3$). In the uni-axial compression loading of GPC, self stress generated in gypsum phase (σ_{sg}) must exhibit the same function as lateral pressure in the tri-axial compression test. So, apparent compressive strength of GPC is increased by the self stress regardless of any contribution of polymer phase.

Therefore, compressive strength of GPC (σ_c) that is strikingly improved by impregnation can be expressed as:

$$\sigma_c = \sigma_{gc} + C_{sg} + C_{pl}, \tag{12}$$

where σ_{gc} = compressive strength of gypsum base, C_{sg} = strength increment derived from tri-axial compression effect due to self stress, and C_{pl} = strength increment derived from existence of polymer phase.

If we know the tri-axial compressive strength of gypsum base measured at a lateral pressure equivalent to the self stress in gypsum base (σ_{tc}), the minimum amount of C_{sg} (σ_{gc} is neglected from contribution) is calculated as:

$$C_{sg} = \sigma_{tc} - \sigma_{sg}. \tag{13}$$

Because the tri-axial test is performed for gypsum base without any self stress, self stress (σ_{sg}) in GPC is initially generated in gypsum phase before uni-axial loading.

The term (C_{pl}) can be divided into two contributions independent of each other. One is strength increment derived from crack arresting toughness of polymer (σ_{pl}) and the other is derived from microscopic change in transmitting path of force caused by the existence of polymer phase (σ_{ex}). Referring to Griffith's theory, the former can be evaluated as the contribution of surface energy (γ) of polymer phase, and the latter as the contribution of change in crack length c and modulus of elasticity E caused by impregnation [1].

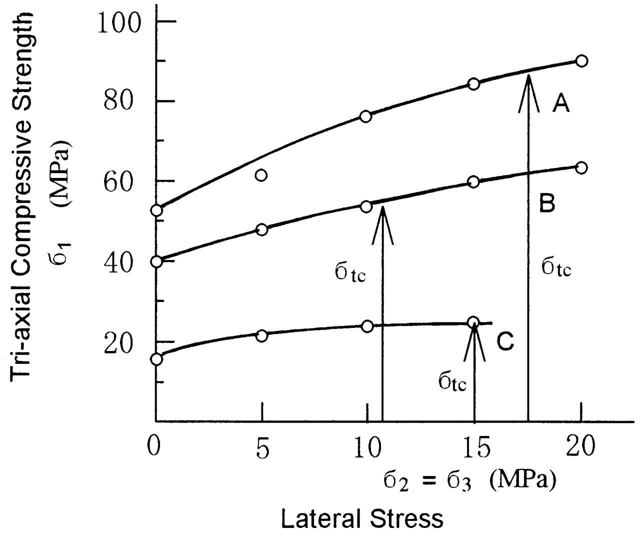

FIGURE 4. Results of tri-axial test of dried gypsum.

Thus, the maximum amount of C_{pl} (if the minimum possible value of C_{sg} is used in eq 12, the value of C_{pl} is possible maximum) is expressed as:

$$C_{pl} = \sigma_{pl} + \sigma_{ex}. \tag{14}$$

Substituting eqs 13 and 14 into eq 12:

$$\sigma_c = \sigma_{gc} + \sigma_{tc} - \sigma_{sg} + \sigma_{pl} + \sigma_{ex} \tag{15}$$

is obtained.

Investigation into Compressive Strength

Results of tri-axial compression test of gypsum base, where dried gypsum base wrapped in a rubber membrane is pressurized laterally and loaded, are shown in Figure 4. Strengths of gypsum bases under lateral stress

TABLE 9. Calculation of polymer contribution

Type of Gypsum	(MPa)				
	σ_c	σ_{gc}	σ_{tc}	σ_{sg}	$\sigma_{pl} + \sigma_{ex}$
A	117.7	52.3	88.5	18.1	−5
B	111.9	26.6	55.1	11.0	41.2
C	84.7	18.2	25.0	15.3	56.8

equivalent to self stress ($б_{sg}$) are obtained as shown in this figure.

Using these values, the maximum contribution of polymer phase ($б_{pl} + б_{ex}$) can be calculated from eq 15 as shown in Table 9. (From eq 12 the maximum value of C_{pl} is obtained if the minimum amount of C_{sg} is assumed.)

For gypsum base A, the maximum contribution of polymer phase ($б_{pl} + б_{ex}$) is found to be negative. Since $б_{ex} > 0$ for positive polymer loading, $б_{pl}$ should be negative for gypsum base A. This means the contribution of crack arresting toughness of polymer to the compressive strength of GPC is also negative for superstressed polymer phase existing in GPC manufactured from gypsum base A.

Conclusion

1. Self stress of GPC can be obtained from shrinkage due to polymerization and modulus of elasticity of base material before impregnation.
2. The self stress generated is balanced in two phases of GPC working as compressive in gypsum phase and tensile in polymer phase.
3. Strength of GPC is affected by self stress, and eq 9 can be applied to predict flexural strength of GPC.
4. The phenomenon that the flexural strength of GPC is decreased after impregnation for gypsum mixed with a small amount of water is interpreted as an unstable physical state where one phase of a composite material is stressed beyond its macroscopic strength due to the crack arresting effect of the other phase. This state is designated as the superstressed state.
5. Tensile superstress existing in polymer phase exhibits such an effect that decreases the apparent compressive strength of composite material. This is consistent with its effect on flexural strength.

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