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Microwave Processing of Glass-Fiber Reinforced Composites—Modification of the Microstructure

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The present article deals with the influence of microwave treatment on the properties of glass-fiber reinforced composites. The cement used in the matrices of the composites was either plain ordinary portland cement or metakaolin-blended cement. Two levels of microwave power were investigated: 40 W and 80 W for 1 hour 30 minutes. The behavior of such composites was compared to that of specimens cured at ambient conditions (20°C) and at 60°C and 90°C. The mechanical behavior was assessed by means of three-point flexure tests. The microstructure was investigated using differential thermal analysis, infrared spectrometry, and scanning electron microscopy. The results obtained show that microwave treatment enhanced the pozzolanic reaction between ordinary portland cement and metakaolin and the bond between the fibers and the matrix. Interfaces between fibers and matrix were also modified. The mechanical performances of the microwave-processed composites were very interesting at early ages, but microwave heating degraded some long-term properties, such as work of fracture and toughness. ADVANCED CEMENT BASED MATERIALS 1997, 6, 116–122.
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[redacted]lass-fiber reinforced composites (GFRCs) are normally of comparatively thin section, manufactured with a lower water/cement ratio than most conventional concretes, and are prone to rapid drying. If this occurs before hydration is complete, the cement never achieves its full strength and the properties of the GFRC are adversely affected, so more attention to curing conditions is necessary.

The details of a curing schedule for GFRC depend on several factors, such as the type of cement used and the mix design, the product, and the manufacturing method used. According to Pilkington's technical data manual [1], GFRC products will achieve a substantial proportion of their ultimate strength when the main cure is carried out for 7 days, in a relative humidity (RH) >95%, and with a minimum temperature of 15°C. It is also good practice to allow the product, following moist curing, to come in equilibrium with the ambient conditions in a gradual manner. Such curing needs important storage areas, especially when large building GFRC façades are manufactured.

In order to reduce the long standard curing period of GFRC products, alternative methods such as increasing the curing temperature or incorporating polymeric materials into the GFRC mixture were suggested [2].

In the present study, another treatment is investigated: microwave curing. Schneider et al. [3,4] used microwave heating to accelerate hydration of cementitious materials. Microwave-treated specimens showed homogeneous structure, high strength, and low porosity compared to identical oven-dried ones. The microwave technique provides a shorter curing period and a better quality of concrete compared with traditional thermal curing. This was confirmed by Xuequan et al. [5,6] and Hutchinson et al. [7].

As heat is generated quickly inside the material, principally from the dielectric losses of water under the electromagnetic field, homogeneous moderate temperatures can be obtained. The power levels needed are quite low, in order to avoid boiling of water.

Microwave curing has been successfully applied to GFRC [8,9]. The present study deals with the influence of microwave treatment on the mechanical performance of GFRC composites and their microstructure.

Experimental

Materials and Sample Manufacturing

GFRC suffers loss in strength and toughness when exposed to the natural environment; therefore, applications are limited to nonstructural purposes. The two main mechanisms leading to strength loss and embrittlement—chemical attack of the glass fibers and

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TABLE 1. Characteristics of metakaolin (MK) and cement (OPC)

Characteristic	MK	OPC
Chemical analysis (w_t %)		
SiO_2	54.3	20.0
Al_2O_3	39.3	4.8
Fe_2O_3	1.5	3.2
CaO	0.0	64.6
MgO	0.0	0.9
K_2O	1.3	0.6
SO_3	0.0	3.3
TiO_2	1.5	0.3
MnO	0.0	0.1
Na_2O	0.0	0.2
P_2O_5	0.0	0.3
LOI	2.1	1.7
Potential composition (w_t %)	Metakaolinite 76.5	C_3S 64.8
	Muscovite 10.3	C_2S 8.5
	Quartz 8.1	C_3A 7.3
	Other phases 5.1	C_4AF 9.7
Fineness		
Blaine specific area (cm^2/g)	ND	4000
BET specific area (m^2/g)	18.7	ND
Average particle size diameter D_{50} (μm)	4.0	12

growth of hydration products around the filaments—have been largely studied [10]. The most widely used solution against the first type of attack is to use alkali-resistant (AR) glass. To counter the second mechanism, Dejean [11] has shown that the addition of metakaolin to the cementitious matrix leads to a time-independent flexural strength.

The binder used in the present study was either plain ordinary portland cement (OPC) or metakaolin-blended cement (MK). The level of cement replacement by metakaolin was 30%. Such an amount of metakaolin leads to the total consumption of calcium hydroxide at 28 days, after an initial microwave treatment, as shown by Péra et al. [8]. The main characteristics of the metakaolin and the cement used in the research are presented in Table 1.

The composite matrix contained 60% binder and 40% fine siliceous sand. The particle size distribution of the sand was in the range of 80 μm to 1 mm.

The water to binder ratio varied from 0.50 (plain OPC) to 0.62 (MK) in order to obtain the same consistency for all composites. Cem-FIL 2, produced by Pilkington Brothers PLC (U.K.), was the AR fiber used in the present study. It presented the following properties: single filament tensile strength 3700 MPa; Young's modulus of elasticity 76 GPa; strain at breaking point 4.9%; thermal stability 400°C to 600°C; filament diameter 20 μm; and filament length 25 mm.

The AR fiber content in the composite was 2.5% by weight.

The composite samples were manufactured using the premix process. They were cast in wooden molds (15 × 40 × 200 mm) and vibrated for 1 minute at 50 Hz. Then the molds were covered by a plastic sheet and placed in the microwave oven.

A 2450-Hz microwave oven (model CEM-MDS 81) was used. The maximum microwave output was fixed at 800 W. Two treatments were applied: (1) 40 W (5% of the maximum power) for 1 hour 30 minutes; and (2) 80 W (10% of the maximum power) for 1 hour 30 minutes.

Higher power levels did not lead to good samples [8,9]. At the end of each treatment, the temperature of the sample was measured; it reached 57°C to 61°C at 40 W and 80°C to 90°C at 80 W.

The behavior of microwave-treated composites was compared to that of samples obtained under the following conditions: (1) 20°C, 90% RH; (2) 1 hour 30 minutes at 60°C, 90% RH; and (3) 1 hour 30 minutes at 90°C, 90% RH.

After demolding, all samples were cured at 20°C, 90% RH for 28 days.

Tests and Analyses

The GFRC samples were tested in three-point bending with a span of 180 mm in an Adamel-Lhomargy machine at a deflection rate of 1 mm/min. The ages at testing were 6 hours, 7 days, and 28 days.

The recording of the load vs. mid-span displacement led directly to the LOP (limit of proportionality), MOR

TABLE 2. LOP of GFRC samples (MPa)

Type of Binder	Age	Type of Treatment				
		5% MW*	10% MW	20°C	60°C	90°C
100% OPC, 0% MK	6 hours	2.0	4.2	0	0.5	1.1
	7 days	4.9	4.2	4.9	5.1	5.3
	28 days	5.5	5.1	5.9	6.2	5.1
70% OPC, 30% MK	6 hours	0.8	3.4	0	0.6	1.0
	7 days	3.8	3.1	2.8	3.6	3.5
	28 days	4.4	4.1	4.9	4.8	4.5

Note: MW = microwave treatment.

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TABLE 3. MOR of GFRC samples (MPa)

Type of Binder	Age	Type of Treatment				
		5% MW	10% MW	20°C	60°C	90°C
100% OPC, 0% MK	6 hours	3.4	5.6	0	1.5	1.9
	7 days	6.8	5.7	7.4	7.4	8.1
	28 days	7.3	6.6	8.7	9.7	8.1
70% OPC, 30% MK	6 hours	1.6	5.4	0	1.6	2
	7 days	5.6	4.7	4.2	6.0	5.5
	28 days	6.2	5.8	7.2	7.7	7.1

(modulus of rupture), and several toughness indices. These indices were those described by ASTM C 1018-85: I_5, I_{10}, and I_{20}. Residual strength factors: $R_{5,10} = 20\ (I_{10} - I_5)$, and $R_{10,20} = 10\ (I_{20} - I_{10})$, were also calculated.

The microstructure was investigated by means of scanning electron microscopy (SEM), differential thermal analysis (DTA), x-ray diffraction (XRD), and infrared (IR) Fourier transform spectrometry.

Results and Discussion

LOP and MOR Values

The LOP and MOR values are presented in Tables 2 and 3 and Figures 1 and 2. Each value is the average obtained from six specimens.

It can be observed that the samples cured at 20°C did not exhibit any strength at 6 hours. At this age, the best

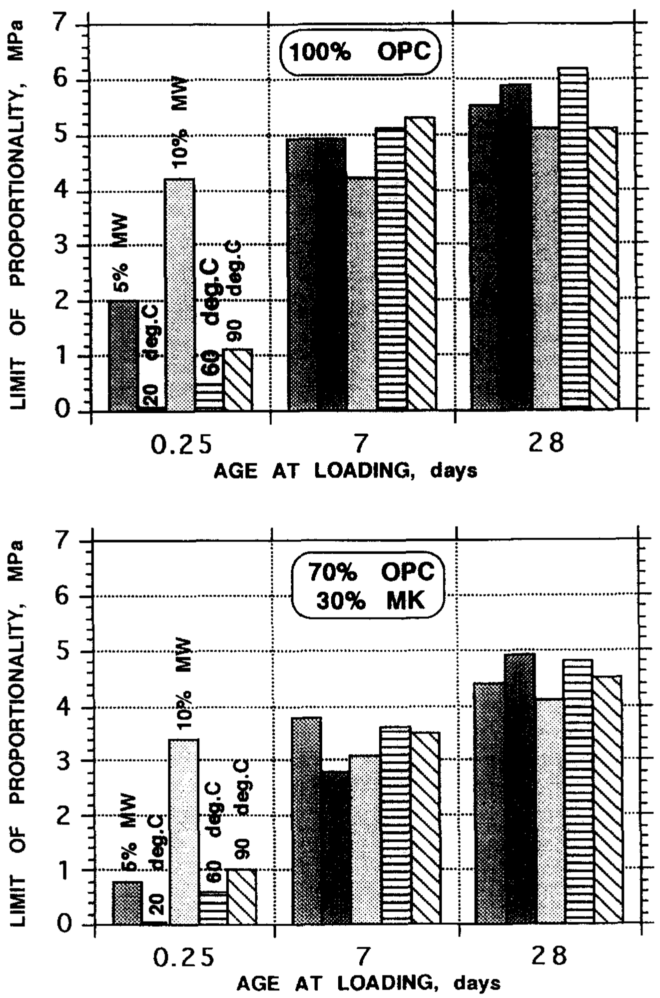

FIGURE 1. Evolution of limit of proportionality with time.

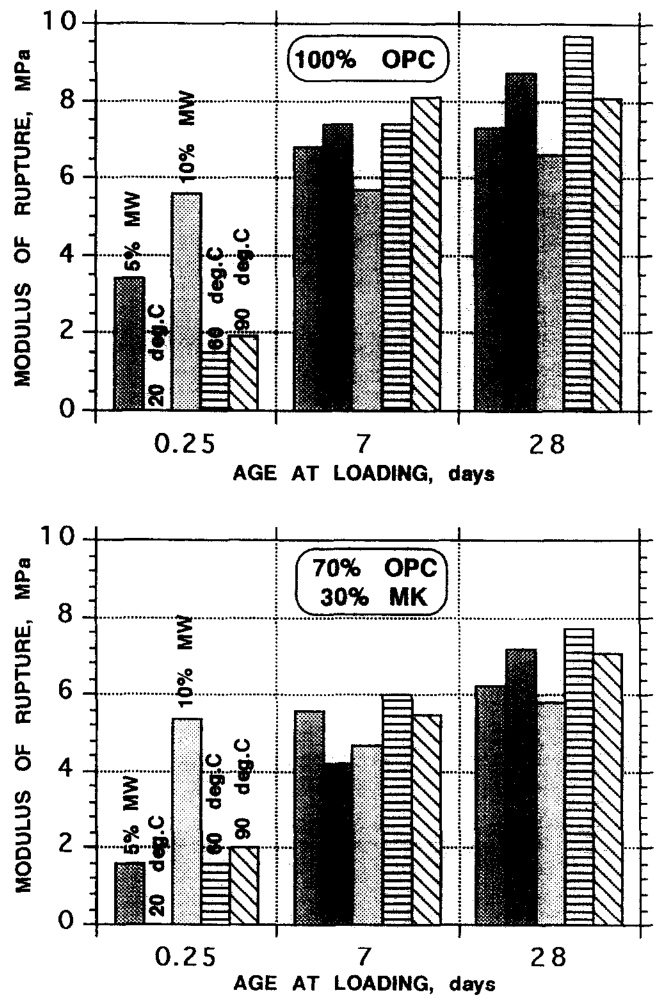

FIGURE 2. Evolution of modulus of rupture with time.

TABLE 4. WOF of GFRC samples (mm.daN)

		Type of Treatment				
Type of Binder	Age	5% MW	10% MW	20°C	60°C	90°C
100% OPC, 0% MK	6 hours	22	24	0	11	9.8
	7 days	18	13	37	27	51
	28 days	11	14.5	30	64	67
70% OPC, 30% MK	6 hours	9	15	0	10	13
	7 days	27	30	23	44	37
	28 days	14	36	22	48	37

LOP and MOR values were obtained for a microwave treatment at 10% of the maximum power. The microwave (MW) treatment at 5% of the maximum power led to the same MOR values as the heat treatment at 60°C or 90°C. The type of cement used did not modify the general trend, even if performance was generally higher with plain OPC.

At 7 days of age, there was no significant difference between the two MW and the two heat treatment regimes. The deviation observed was in the range of 0.6 MPa (LOP values) to 2 MPa (MOR values) with maximum differences of 1.1 MPa for LOP values and 2.4 MPa for MOR values.

At 28 days of age, and for the two binders used, the best performance was obtained for an initial treatment at 60°C or 90°C for 1 hour 30 minutes, followed by a cure at 20°C and 90% RH. The two MW treatments led to lower LOP and MOR values than the curing at ambient conditions (20°C, 90% RH).

The strength performance of MK-based GFRC composites was generally slightly lower than that of plain OPC-GFRC; this could be explained by the higher amount of water used (0.62 for OPC/MK = 70/30 instead of 0.50 for plain OPC). However, the difference between the two binders decreased with time: at 7 days, the MK-GFRC presented average MOR values 26% lower than those of the OPC-GFRC; at 28 days, this difference was only 16%. This result also proves the effectiveness of the pozzolanic reaction between metakaolin and cement. The values presented in Table 3 and Figure 2 also show that the MW treatment at 10% of the maximum power accelerated the pozzolanic reaction. For such treatment, the difference between the MOR values at 7 and 28 days for MK-GFRC and OPC-GFRC was 17.5% and 12%, respectively. At 90°C, the difference was 32% and 12%, and at 20°C, it reached 43% and 17% respectively. The above results also suggest that the MW treatment at 10% of the maximum power and the heat treatment at 90°C are not equivalent: the pozzolanic reaction starts sooner as the MW treatment is used.

Work of Fracture

The work of fracture (WOF) values corresponding to the MOR values are shown in Table 4 and Figure 3.

For plain OPC with MW treatment, the work of fracture up to MOR was very high at early age (6 hours). However, it strongly decreased with time. On the other hand, the treatments at 60°C and 90°C led to increasing values of WOF with time, and at 28 days were better than a cure at 20°C.

The results obtained for MK-GFRC did not follow the same trend. At 6 hours of age, the MW and heat treatments were equivalent. At 7 days, the specimens

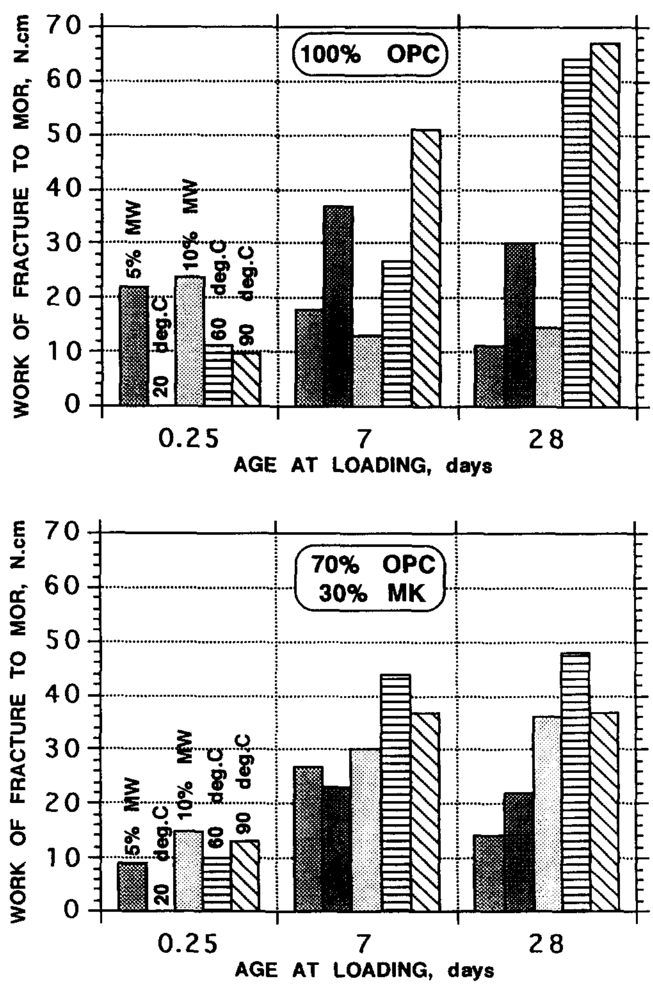

FIGURE 3. Evolution of work of fracture to modulus of rupture (MOR) with time.

TABLE 5. Toughness indices and residual strengths

Type of Binder	Type of Treatment	Age	Toughness Indices I_5	I_{10}	I_{20}	Residual Strengths $R_{5,10}$	$R_{10,20}$
100% OPC, 0% MK	5% MW	6 hours	5.1	11.0	23.3	297	124
		7 days	5.6	11.4	20.0	115	86
		28 days	6.0	10.7	15.3	95	46
	10% MW	6 hours	5.3	10.4	20.2	102	98
		7 days	5.7	11.6	17.2	118	56
		28 days	5.6	10.2	15.4	93	52
	20°C	6 hours	0	0	0	0	0
		7 days	6.2	13.1	25.7	138	126
		28 days	6.0	13.2	20.2	144	70
	60°C	6 hours	6.3	16.5	36	204	196
		7 days	5.7	12.4	22.2	135	97
		28 days	5.8	12.7	22.9	138	102
	90°C	6 hours	6.2	14.1	29.8	157	157
		7 days	5.7	12.6	26.5	139	138
		28 days	6.2	14.0	28.4	156	144
70% OPC, 30% MK	5% MW	6 hours	6.9	16.3	35.1	190	187
		7 days	5.9	12.6	23.8	133	112
		28 days	6.3	11.4	15.5	101	41
	10% MW	6 hours	6.6	15	26.4	168	114
		7 days	6.2	13.3	24	142	105
		28 days	5.3	11.5	22.1	122	106
	20°C	6 hours	0	0	0	0	0
		7 days	5.8	13	26.6	143	136
		28 days	6.1	11.8	16.4	114	46
	60°C	6 hours	6.3	16.2	39.3	196	231
		7 days	6.3	14.6	29.8	166	152
		28 days	6.1	13.5	21.4	147	79
	90°C	6 hours	6.3	15.2	34.3	177	191
		7 days	5.7	12.7	27.4	141	146
		28 days	5.8	12.6	20.6	135	90

treated at 60°C and 90°C developed higher WOF values than MW-treated samples. Also, the WOF values were higher than those observed at 6 hours. At 28 days, the best treatment was that at 60°C, which led to higher values than at 7 days. Heating at 90°C preserved the values obtained at 7 days, as did the MW treatment at 10% of the maximum power and the curing at 20°C.

From Table 4 and Figure 3, it can be concluded that MW treatment strongly affects the long-term ductility of OPC based composites. Such treatment is less ad-

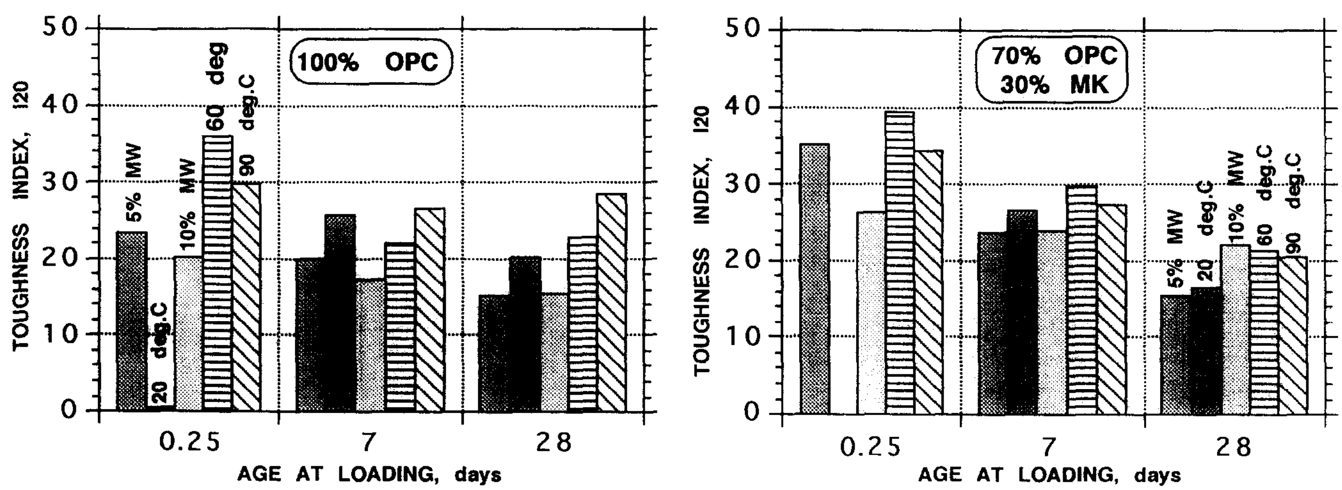

FIGURE 4. Evolution of the toughness index I_{20} with time.

TABLE 6. Evolution of the DTA peak of CH (A.U)

		Type of Treatment				
Type of Binder	**Age**	**5% MW**	**10% MW**	**20°C**	**60°C**	**90°C**
100% OPC, 0% MK	7 days	397	285	420	400	400
	28 days	355	290	355	320	340
70% OPC, 30% MK	7 days	70	0	97	110	105
	28 days	16	0	27	30	35

verse in MK based composites. However, in each case, the recommended treatment of GFRC composites seems to be initial heating at 60°C for 1 hour 30 minutes, followed by a cure at 20°C and 90% RH.

Toughness Indices and Residual Strengths

The different toughness indices (I_5, I_{10}, I_{20}) and the residual strengths $R_{5,10}$ and $R_{10,20}$ are presented in Table 5 and Figure 4 (I_{20}).

Indices I_5 and I_{10} were always higher than 5 and 10 (except at 6 hours, 20°C, 90% RH), whatever the binder and the treatment was. Index I_{20} was higher than 20 at 28 days, for the following conditions: (1) OPC-GFRC: thermal treatment at 20°C, 60°C, and 90°C; and (2) MK-GFRC: MW treatment at 10% of the maximum power, or heating at 60°C and 90°C.

Long-term ductility, which means residual strengths $R_{5,10}$ and $R_{10,20}$ higher than 100, was obtained for the following conditions: (1) OPC-GFRC: thermal treatment at 60°C and 90°C; and (2) MK-GFRC: MW treatment at 10% of the maximum power, heating at 60°C and 90°C.

From Table 5 and Figure 4, it can be concluded that MW treatment decreases the long-term ductility of OPC-GFRC. This embrittlement is not due to the water loss occurring during the treatment, which remained <0.1%. A parallel microstructural investigation showed that a modification of interfaces between fibers and matrix took place during the MW treatment.

Microstructure

The main hydrates formed during the microwave treatment were C–S–H, ettringite, and portlandite, as shown by DTA, XRD, and IR spectrometry. In the MK-modified matrix, the quantity of ettringite was reduced and monosulphate appeared; strätlingite (C_2ASH_8) was also present. The evolution of the portlandite content is given in Table 6. The measurement was not done at 6 hours of age because all the samples were not hardened.

The microwave treatment (10% MW) accelerated the lime consumption by metakaolin: the composite did not contain any remaining portlandite at 7 days [12]. The treatment at 60°C or 90°C gave about the same lime consumption as the curing at ambient temperature.

SEM examinations were done on GFRC samples cured at 20°C or treated at 10% MW, after 28 days of hydration. In the plain OPC matrix, it was observed that portlandite crystals were larger when the composite was cured at 20°C, which confirms the results of Skalny and Young [13]: the modification of solubilities as the temperature increases leads to the precipitation of a larger proportion of small $Ca(OH)_2$ crystals.

At 20°C, more portlandite and ettringite precipitated

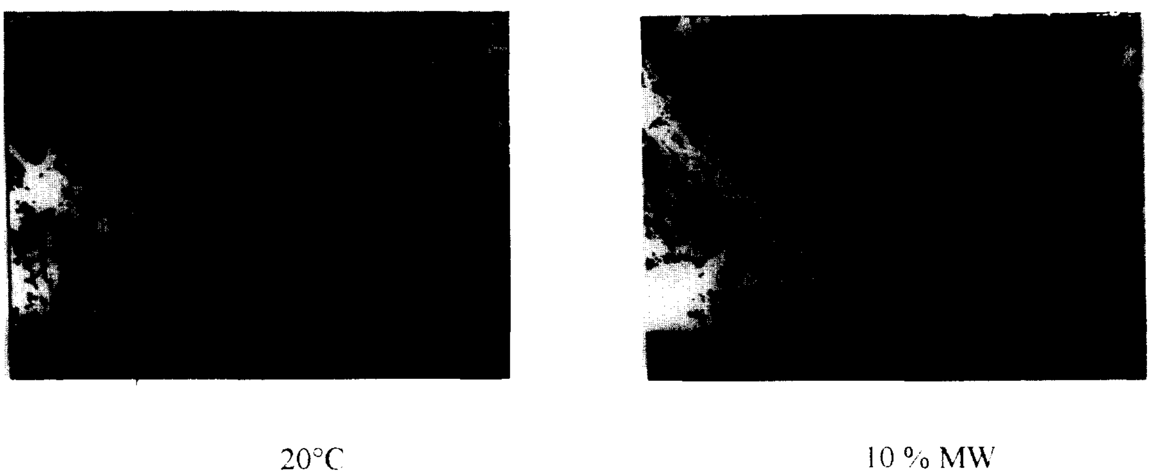

FIGURE 5. SEM micrographs of fiber-matrix interfaces in plain OPC-GFRC.


20°C


10 % MW

FIGURE 6. SEM micrographs of fiber impress in the MK-modified matrix.

at the fiber-matrix interface than in the microwave-treated specimens (Figure 5).

The potassium ions that were present in the C–S–H close to the fiber when the sample was cured at 20°C were better dispersed in the matrix by the microwave treatment. Under such treatment, these ions did not migrate toward the fiber.

In the MK-modified matrix, the same result was found when the matrix was microwave treated. Interfaces were modified by the microwave treatment, as shown in Figure 6. In the GFRC cured at 20°C, C–S–H was present mainly at interfaces, while crystals of strätlingite and monosulphate were detected at 10% MW.

No portlandite was found after the microwave treatment, but unreacted MK remained in the matrix. The better crystallization of the matrix can explain the embrittlement of the composite, as the fiber is blocked by the crystals and no longer can slip in the matrix.

Conclusion

The microwave treatment of GFRC leads to better early strengths (at 6 hours of age) than an equal time cure at 60°C or 90°C. Therefore, demolding is made easier. Such treatment also accelerates the pozzolanic reaction between metakaolin and portlandite but embrittles the composite. More crystallized products, i.e., strätlingite and monosulphate, precipitate at the fiber-matrix interfaces, preventing the fiber from slipping in the matrix and therefore limiting the ductility of the composite.

The recommended treatment of GFRC seems to be initial heating in the range of 60°C to 90°C for 1 hour 30 minutes, followed by a cure at 20°C and 90% RH.

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