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Structural properties of sepiolite-reinforced cement composite

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Abstract

The structural properties and optimum blend ratios of sepiolite-reinforced cement composites are investigated. It is shown that the addition of 10% sepiolite (a natural clay mineral) fibers enhances the mechanical and physical properties of the mortar. In comparison to the ordinary Portland cement mix, improvements of 3.5%, 6.2% and 7.7% in compressive strength and 12.7%, 5.7% and 6.3% in bending strength values were respectively obtained for 2, 7 and 28 days. Based on the scanning electron microscope pictures, this enhancement is attributed to the modification of the rheology of the mortar through sepiolite fibers inducing a network structure within the cement matrix.
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1. Introduction

Concrete is a hydraulic bond which contains cement, water and aggregates. When irregular fibrous materials, natural or synthetic in nature, are added into concrete, it is called fiber-reinforced concrete (FRC). In the construction industry, which has undergone a very rapid development period since the 1980s, fiber-reinforced precast concrete products have been fulfilling an important task for both designers and contractors by offering technical and aesthetic conveniences. Because of the health problems it caused, asbestos, once widely used as a provider of fibrous structure, left its place to fibrous synthetic materials. Today, steel, glass or plastic fibers in various lengths, geometrical shapes and thicknesses are used in the production of FRC [1]. However, because asbestos fibers exhibited outstanding properties, such as high elasticity modulus, resistance to high temperatures and chemicals, noncombustibility, stability at high pH as well as price advantages, [2], the search to substitute asbestos continues [3]. Table 1 illustrates typical properties of fiber and cement matrix [1].

A large number of fibers in adequate length and small diameter is required for the production of sufficient strength and elasticity. Addition of 0.4–3% fiber by volume is found to result in significant improvements in bending strength and fracture behavior of the concrete [4]. Ordinary concrete has a low level of tensile strength (<4 N/mm^2) under very high compressive strengths of 25–100 N/mm^2. The existing stress has to be compensated by building components of adequate tensile strength. FRC delays the propagation of cracks occurring in the structure and improves the tensile strength, flexural strength and impact resistance properties of concrete. Such characteristics produce numerous but small and less hazardous cracks instead of few but large cracks during loading process. Fiber-strengthened concrete can meet even higher tensile strengths by means of fibers of greater elasticity even after the cement is removed from the aggregate. FRC does not have the same properties as ordinary concrete which shows sudden fragility characteristics under overloaded conditions. Calcination studies of sepiolite conducted at 830 °C indicate that sepiolite-mixed mortar can yield compressive strengths up to 84% compared to that of the reference ordinary Portland cement [5,6].

The primary objective of this study has been to investigate the effect of adding a natural fibrous clay mineral, as an alternative to asbestos, to a mixture of Portland cement

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Table 1
Properties of fibers and cement matrix [1]

Fiber	Diameter (μm)	Specific gravity (g/cm^3)	Modulus of elasticity (kN/mm^2)	Tensile strength (kN/mm^2)	Elongation at break (%)
Asbestos	0.02–20	2.55	165	3–4.5	2–3
Glass	9–15	2.60	70–80	2–4	2–3.5
Graphite	8–9	1.90	240–415	1.5–2.6	0.5–1.0
Steel	5–500	7.84	200	0.5–2.0	0.5–3.5
Polypropylene	20–200	0.91	5–77	0.5–0.75	20
Aromatic polyamide	10	1.45	65–133	3.6	2.1–4.0
Sisal	10–50	1.50	–	0.8	3.0
Cement matrix	–	2.50	10–45	$3–7 \times 10^{-3}$	0.02

clinker and gypsum to produce a fiber-reinforced cement sample and assess its quality through physical and mechanical tests.

2. Characteristics of sepiolite

Sepiolite is a microcrystalline-hydrated magnesium silicate with $Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$ as the unit cell formula [7]; it exhibits a microfibrous morphology with a particle length of 2–10 μm. Structurally, it is formed by an alternation of blocks and tunnels which grow up in the fiber direction. Each structural block is composed of two tetrahedral silica sheets sandwiching a central sheet of magnesium oxide–hydroxide [8]. This unique structure imparts sepiolite a fibrous matrix with channels (3.6 × 10.6 Å) oriented in the longitudinal direction of the fibers. The fibrous structure of sepiolite induces sorptive, colloidal/rheological and catalytic properties, which find a variety of diverse applications. The fiber length, width and thickness of layered sepiolite as bundles of fiber can range between 100 Å and 5 μm, between 100 and 300 Å and between 50 and 100 Å, respectively. However, the length of fibers in sepiolite varies according to the source of sepiolite [9]. For example, the length of Ampandrandawa and China sepiolites reaches up to a few millimeters, and sometimes even a centimeter. While the fiber dimensions of Vallecas (Spain) sepiolite are 8000 × 250 × 40 Å [10], the fiber length of the original brown sepiolite from Türktaciri region of Turkey is determined as 5–10 μm [11].

Sepiolite exhibits a porous structure. While an average micro pore diameter is measured as 15 Å, mezzo pore radius ranges between 15 and 45 Å. Its density typically varies in the range of 2–2.5 g/cm^3, but that of more porous types may go down to as low as 1 g/cm^3 [12].

3. Experimental

The brown sepiolite sample of 90% in purity and 8% humidity from Sivrihisar–Eskişehir region was supplied by Koray Industrial Minerals. The mineralogical analysis determined by X-ray diffraction (XRD), together with optical microscopy, reveal that dolomite is the major associated impurity with traces of quartz, calcite and clay minerals. In addition to sepiolite, 5% gypsum and ordinary Portland cement clinker manufactured by Afyon Set Cement Factory were added to the mixture of FRC sample. The control sample (Sample 1) did not contain any sepiolite. Sepiolite in proportions of 3, 5, 10, 15, 20 and 30 by weight was added to the cement mixture for the production of FRC. The control sample and other mixtures (Samples 2, 3, 4, 5, 6 and 7) composed of the Portland cement clinker, gypsum and sepiolite in desired proportions were crushed to −2.5 mm by a laboratory-type crusher and then ground to the same fineness until the residue at a 40-μm sieve was 20 ± 1%. The chemical analyses of sepiolite and other mixtures performed by XRF method are presented in Table 2. The chemical, physical and mechanical tests on ground samples were performed according to TS 687 [13] and TS 24 [14].

The properties of the control sample were compared and evaluated with those of sepiolite-blended cement samples using the residues on 40-, 90- and 200-μm

Table 2
Chemical analyses of sepiolite-reinforced cement at different sepiolite additions

No.	Clinker (%)	Sepiolite (%)	Gypsum (%)	SiO_2[a] (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	K_2O (%)	Na_2O (%)	LOI (%)	Ins. Res. (%)
	100	–	–	21.24	4.80	3.15	65.27	2.50	0.83	0.87	0.25	0.30	–
	–	100		35.55	2.85	1.42	13.06	18.59	0.46	0.64	0.07	26.4	–
	–	–	100	6.89	0.80	0.24	32.05	0.99	39.65	0.07	0.02	19.00	–
1	95	0.0	5.0	21.08	4.58	3.00	63.63	2.49	2.72	0.84	0.25	1.20	0.85
2	92	3.0	5.0	21.07	4.66	2.93	62.72	2.90	2.72	0.82	0.25	1.73	0.90
3	90	5.0	5.0	21.11	4.73	2.98	61.65	3.26	2.69	0.80	0.23	2.36	3.20
4	85	10.0	5.0	21.70	4.74	2.82	59.37	3.91	2.65	0.77	0.26	3.35	4.97
5	80	15.0	5.0	22.28	4.64	2.78	57.19	4.42	2.52	0.77	0.23	4.87	4.03
6	75	20.0	5.0	22.60	4.59	2.68	54.73	5.45	2.60	0.75	0.25	6.08	5.40
7	65	30.0	5.0	23.41	4.56	2.57	50.38	6.70	2.52	0.71	0.27	8.72	6.14

[a] Total SiO_2.

Table 3
Physical tests applied to cement samples blended with sepiolite

No.	% Sieve residue			Blaine (cm^2/g)	H_2O (%)	Soundness (mm)
	40 μm	90 μm	200 μm			
1	20.1	1.0	0.0	3508	26.4	8
2	20.6	1.2	0.0	3879	26.4	7
3	20.4	1.1	0.0	4202	26.6	5
4	19.4	1.1	0.0	4612	26.6	7
5	20.5	1.5	0.1	4996	27.0	3
6	19.7	2.0	0.1	5554	27.6	4
7	19.3	3.6	0.2	5891	27.6	4

sieves, Blaine-specific surface areas, initial and final setting times, compressive and bending strength values and water demand (W/C; water/cement ratio in the mortar tests for strength was maintained at 0.5) expansion volume.

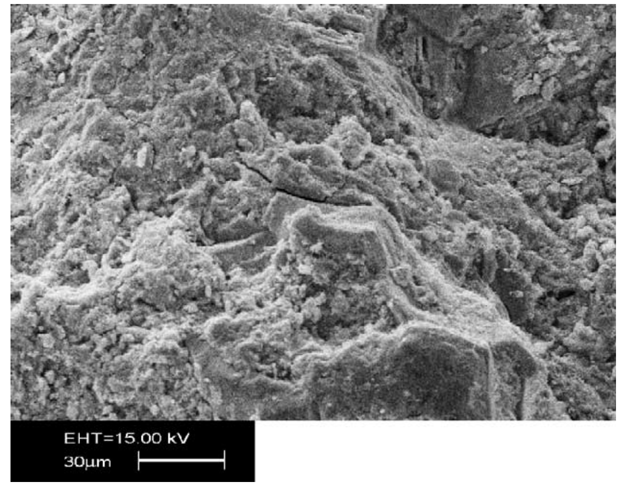

Fig. 1. SEM photomicrograph of a typical Portland cement mortar.

4. Results and discussion

The effect of sepiolite as an additive in increasing proportions is summarized in Tables 2–4 using chemical, physical and mechanical test results of the samples. When Table 2 is examined, no distinct changes are observed in chemical analysis results upon addition of sepiolite except for LOI and insoluble residues at and above 15% sepiolite addition. Water demand (W/C) presented in Table 3 remains stable even at the highest sepiolite addition. The internal zeolitic channels and external silanol (Si–OH) groups by hydrogen bonding in sepiolite help retain a significant amount of water.

Soundness (expansion volume) given in Table 3 decreases with the addition of sepiolite, indicating its favorable effect. Because sepiolite is characterized by molecular sieve properties, its addition leads to a substantial increase in surface areas, as seen in Table 3. However, as apparent in Table 4, despite a progressive decrease in clinker content, the addition of sepiolite up to 10% improved the compressive and bending strengths of the mortar. This improvement cannot be ascribed to the increase in specific surface area because a further increase in sepiolite addition led to a decrease in compressive and bending strength values despite an increase in Blaine values in Samples 5, 6 and 7. The reason for the deterioration of compressive and bending strength values above 10% sepiolite addition can be attributed to the dilution effect of clinker which forms the main matrix. Sepiolite in this study was used as an additive and the other major components, i.e., clinker, were progressively diluted. In spite of a reduction in the clinker addition, a systematic improvement in the strength values was observed because of the shape and pozzolanic activity of sepiolite. The effect of pozzolanic activity on the strength values usually does not appear before the 28-day period, as apparent in Table 4, despite controversy in the literature [15].

Evidently, the lower addition of sepiolite, i.e., Samples 2 and 3, does not improve much the compressive and bending strengths of the cement matrix. This indicates that an optimum fiber distribution is required to achieve a network

Table 4
Mechanical tests applied to cement samples blended with sepiolite

No.	Setting time (min)		Compressive strength (N/mm^2)			Bending strength (N/mm^2)		
	Initial	Final	2-day	7-day	28-day	2-day	7-day	28-day
1	156	240	20.0	32.5	41.7	4.7	7.0	8.2
2	132	252	19.6	33.2	42.8	4.6	7.0	8.4
3	162	246	20.1	33.3	43.4	4.8	6.9	8.5
4	108	216	20.7	34.5	44.9	5.3	7.4	8.7
5	204	348	18.9	32.6	42.7	4.6	6.7	7.8
6	204	312	15.7	29.2	40.2	3.9	6.2	7.9
7	306	432	11.2	23.2	31.5	2.8	5.2	6.6

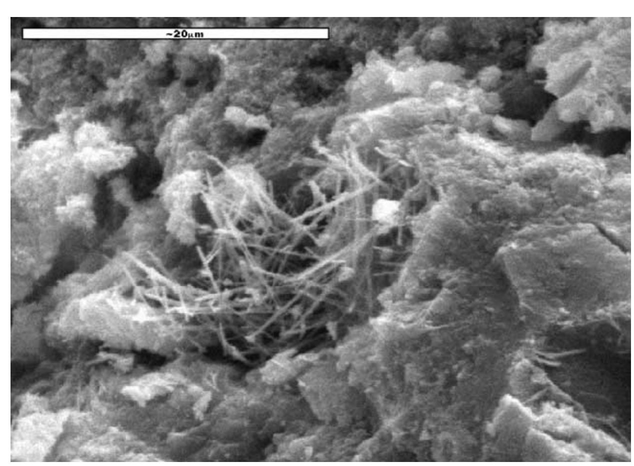

Fig. 2. SEM photomicrograph of sepiolite-reinforced cement mortar taken from a different point.

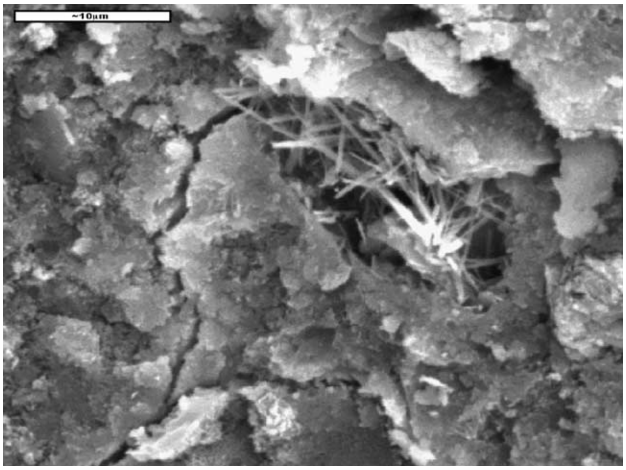

Fig. 3. SEM photomicrograph of sepiolite-reinforced cement mortar taken from a different point.

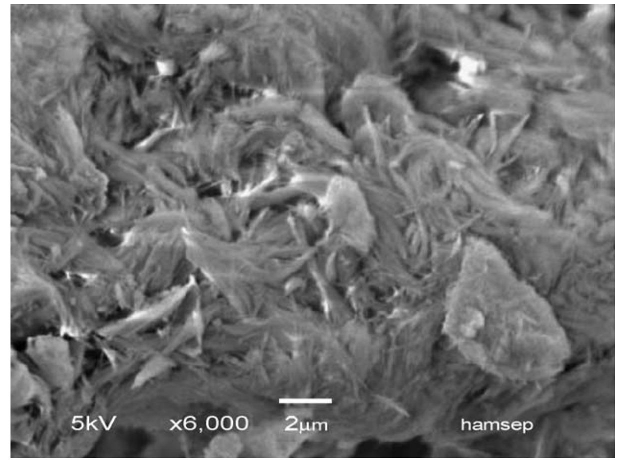

Fig. 5. SEM photomicrograph showing the fibrous structure of sepiolite samples.

structure of fibers in the cement matrix. As seen in Fig. 2, the fibrous sepiolite particles have penetrated into the pores of cement paste (Fig. 1) and by absorbing some of the water molecules, it delayed the setting times. In addition, as the sepiolite content is increased, the proportion of C3A phase is decreased with a corresponding increase in setting times. This is evident in Table 4 for Samples 5, 6 and 7. The distribution of fibers in the pores is shown more vividly in Figs. 2–4.

The nucleation and fatigue cracking in concrete are attributed to the inherent weakness of concrete under tension. Incorporation of fibers into concrete in this way improves its mechanical behavior [16,17] and leads to a reduced shrinkage [18]. The weak surface load of sepiolite, together with the absence of swelling and the needle shape of its particles, confers a singular rheological behavior on this material. Addition of sepiolite slows down the rate of carbonation process due to its ability to adsorb water [19]. The adsorption of $Ca(OH)_2$ to the chrysotile (an asbestos mineral) fibers indicated that the hydration heat reactions are intensified in the presence of asbestos $Mg_3Si_2O_5(OH)_4$ through active 1018 centers per cm^2 [2]. In this respect, sepiolite has much higher surface areas and consequently more active centers than asbestos and thus higher ability to adsorb calcium compounds in cement.

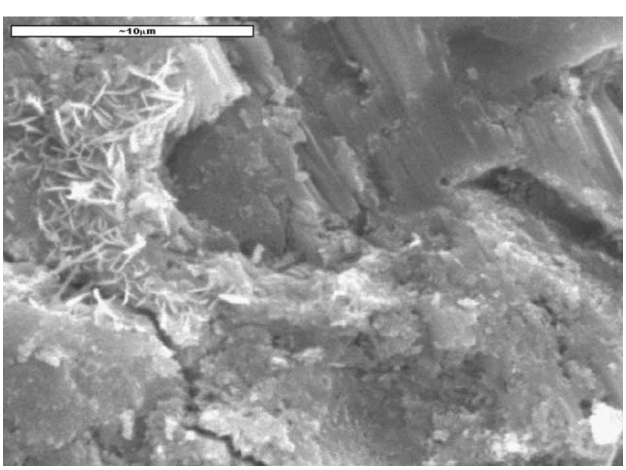

Fig. 4. SEM photomicrograph of sepiolite-reinforced cement mortar taken from a different point.

While the SEM image of sepiolite fibers is illustrated in Fig. 5, the structure of cement upon 10% sepiolite addition is given in Figs. 1 and 2. Apparently, the sepiolite fibers fill the cavities in the cement mortar leading to the favorable effects on compressive and bending strengths. These pictures provide sufficient evidence that sepiolite fibers impart a network structure and may regulate the rheological properties of the cement mortar.

5. Conclusions

Although natural pozzolanic additives are generally known to reduce particularly the early compressive and bending strengths of the cement, the addition of 10% sepiolite is found to increase both the compressive and bending strengths of the mortar strength. The results of the mechanical and physical tests along with SEM pictures indicated that sepiolite fibers distributed within the cement matrix is expected to modify the rheological properties of the cement mortar and in turn impede the expansion of cracks during the fracture. Research is in progress to identify the effect of fiber length of sepiolite and more importantly, that of sepiolite content. Natural sepiolite with its fibrous structure, high volume stability and considerable chemical and structural stability in strongly alkaline medium is expected to open new avenues in the use of fiber materials in cement.

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