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Effect of 3-Chloro-2-Chloromethyl-1-Propene Modified Polypropylene Fibers on Compressive Strength Performance in Cementitious Systems

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Abstract

The service life of cementitious systems is reduced as a result of the different environmental effects to which it is exposed. In order to increase the performance of cementitious systems, chemical-mineral additives and fibers are added to the systems in question. While fibers absorb some of the stresses formed in the paste phase of the cementitious system, they transfer some of them to the more durable region of the matrix, limiting crack propagation. Various studies are carried out to increase the adhesion of fibers to the cementitious paste-fiber interface. The most common of these is to change the fiber shape and surface roughness with the help of mechanical processes. For example, improving the fiber-concrete matrix interface by hooking and bending processes is a widely preferred method. In this way, the bond strength can be significantly increased. However, these measures can reduce the stiffness of the fibers themselves. In addition, hooking and bending processes can be problematic in terms of their applicability to microfibers. In addition to physical modifications, chemical processes can also be performed to create a high-affinity fiber-matrix interface. In this study, surface modification was applied to the surface of 6 and 12 mm long polypropylene fibers with 3-Chloro-2-Chloromethyl-1-Propen chemical. In this context, mortar mixtures were prepared by changing modified and unmodified fibers by 0.5% of the aggregate volume. In all mortar mixtures, water/cement, sand/binder and spreading values were kept constant as 0.485, 2.75 and 200±20 mm, respectively. In order to provide the desired flow value, a single type of polycarboxylate-ether based high-level water-reducing additive was added to the mixtures at different rates. CEM I 42.5 R type cement and crushed limestone aggregate were used in all mixtures. According to the obtained results, adding fiber to the mixture and increasing the fiber length, regardless of the fiber type, increased the need for water-reducing additive for the target workability value. Surface activation of 3-chloro-2-chloromethyl-1-propene slightly improved the workability in short fibers, while no significant effect on spreading was observed in long fibers. Surface activation had no significant effect on compressive strength.

Keywords: Modified Polypropylene Fibers, mechanical performance, cementitious systems, 3-Chloro-2-Chloromethyl-1-Propene

1. Introduction

The brittle behavior of cementitious systems can cause various structural damages [1]. In order to increase the performance of these systems, fiber reinforcement is applied together with chemical and mineral additives. Fibers limit crack propagation by absorbing some of the stresses formed in the dough phase of cementitious systems and transferring some of them to more durable regions [2]. While macro fibers improve mechanical performance by creating a bridging effect in the matrix, micro fibers are widely used to prevent the formation of micro cracks. It has been determined that micro-sized glassy, synthetic, carbon, basalt and steel fibers are used to increase the durability performance of cementitious systems [2,3]. Steel fibers are generally preferred in structural systems such as floors and tunnels where high rigidity is required and flexural strength is critical [4]. However, steel fibers are sensitive to aggressive environmental conditions. For this reason, the use of synthetic fibers is becoming widespread in cementitious systems where durability performance is at the forefront [5]. Various surface modifications can be applied to increase the hydrophilicity and chemical reactivity of synthetic fibers [6,7]. Although different raw materials and processing technologies are used, the common strategy of these studies generally focuses on the addition of polar functional groups containing oxygen atoms to the fiber surface [8,9]. In this study, surface modification was applied to the surface of 6 and 12 mm long polypropylene fibers with 3-Chloro-2-Chloromethyl-1-Propene chemical. In this context, mortar mixtures were prepared by replacing modified and unmodified fibers at a rate of 0.5% of the aggregate volume. The effect of modified fibers on the mechanical performance of cementitious systems was examined.

2. Materials and Methods
2.1. Materials
Cement

In this project, CEM I 42.5 R type cement, which complies with TS EN197-1 standards, was used in the mortar. The physical, chemical and mechanical properties of the cement are given in Table 1.

Table 1. Physical, chemical and mechanical properties of cement

Oxide (%)	Cement	Physical Properties		
SiO_2	18.86	Özgül Ağırlık		3.15
Al_2O_3	5.71	**Fineness**		
Fe_2O_3	3.09	Özgül yüzey (Blaine, cm^2/g)		3530
CaO	62.70	0.045 mm residue on the sieve (%)		7.6
MgO	1.16	**Mechanical Properties**		
SO_3	2.39	Compressive Strength (MPa)	1-Day	14.7
Na_2O+0,658 K_2O	0.92		3-Day	26.80
Cl'	0.01		7-Day	49.80
Insoluble residue	0.32		28-Day	58.5
Loss of ignition	3.20			
Free CaO	1.26			

Aggregate

River sand aggregate with a grain diameter of 0-4 mm was used in the production of mortar mixtures. According to the TS EN 1097-6 standard, the saturated surface dry specific gravity of the aggregate was measured as 2.64 and the water absorption capacity was measured as 0.4%.

Water Reducing Admixture

A single type of polycarboxylate based high-rate water reducing admixture was used to provide the targeted spreading and slump values in mortar mixtures. Some of the properties of the water reducing admixture used, provided by the manufacturer, are given in Table 2.

Table 2. Chemical properties of water reducing admixtures

Properties	Values
Density (gr/cm^3)	1,073
Chemical compound	Polycarboxylate based liquid
Solid content (%)	28,76
Chlorine content (% kütlece)	0,0618
Alkali content (% kütlece)	≤4
pH (%10 solution)	4,89

Polypropylene Fiber

PP fibers used in the study were produced by recycling daily waste. After melting waste PP materials at high temperatures, they are turned into raw PP granules. After the granulated PPs are processed again, they are turned into fibers of 6 mm and 12 mm length. The appearance and properties of PP fibers are given in Figure 1 and Table 3. Surface activation was applied to PP fibers by chemically modifying the surface with 3-Chloro-2-Chloromethyl-1-Propene.

Figure 1. Image of PP fibers

Table 3. Physical Properties of PP fibers

	Fiber length (cm)	Fiber diameter (µm)	Specific gravity
PP fiver	6 mm and 12 mm	18-20	0,91

2.2. Method

Polypropylene Fiber Modification Process

10 g PP and 20 mL distilled water were combined with 2 g 3-Chloro-2-Chloromethyl-1-Propene and dissolved in ethanol to prepare a homogeneous solution. The solution was transferred to the second glass reactor. 0.1 g benzoyl peroxide (BPO) radical initiator was added to the solution. PP fibers were added to the reactor and this mixture was mixed for 5 h at different mixing speeds and temperature ranges (not exceeding 60°C). Mixing was continued at 25°C for 24 h.

Figure 2. Beginning of Synthesis

2.3. Preparation of Mixtures

Mortar mixtures were produced according to ASTM C109 standard. In all mixtures, water/binder ratio and spreading amount were kept constant as 0.485 and 190±20 mm, respectively. In mixtures containing fiber, fiber was replaced with aggregate by volume at 0.50% of the total volume. In order to provide the desired spreading values in mortar mixtures, a single type of polycarboxylate-ether based high-rate water-reducing admixture was used at different dosages. Mortar mixture calculations were made for 1 dm3 volume.

The mixing process was carried out with the help of a cement mixer according to ASTM C305 standard. First, after adding cement to water, mixing was carried out at 140 rpm (slow) for 30 seconds. Then, sand and fiber were added to the cement paste and mixing was carried out at 140 rpm for 30 seconds, then it was mixed at 285 rpm for 30 seconds. The mixer was stopped and the mixture was left to stand for 90 seconds. During this process, the sides of the mixer bowl were scraped within the first 15 seconds. After the water-reducing chemical additive was added, the mortar mixture was mixed for another 60 seconds at 285 rpm.

2.4. Mortar Fresh State Tests

The spreading value of the produced mortar mixtures was determined according to the ASTM C1437 standard.

2.5. Hardened Mortar Tests

The bending and compressive strengths of 28-day 4x4x16 cm mortar samples were determined according to the TS EN 196-1 standard.

3. Results and Discussion

3.1. Characterization of fibers

Characterization of the modified fiber is given in Figure 3.

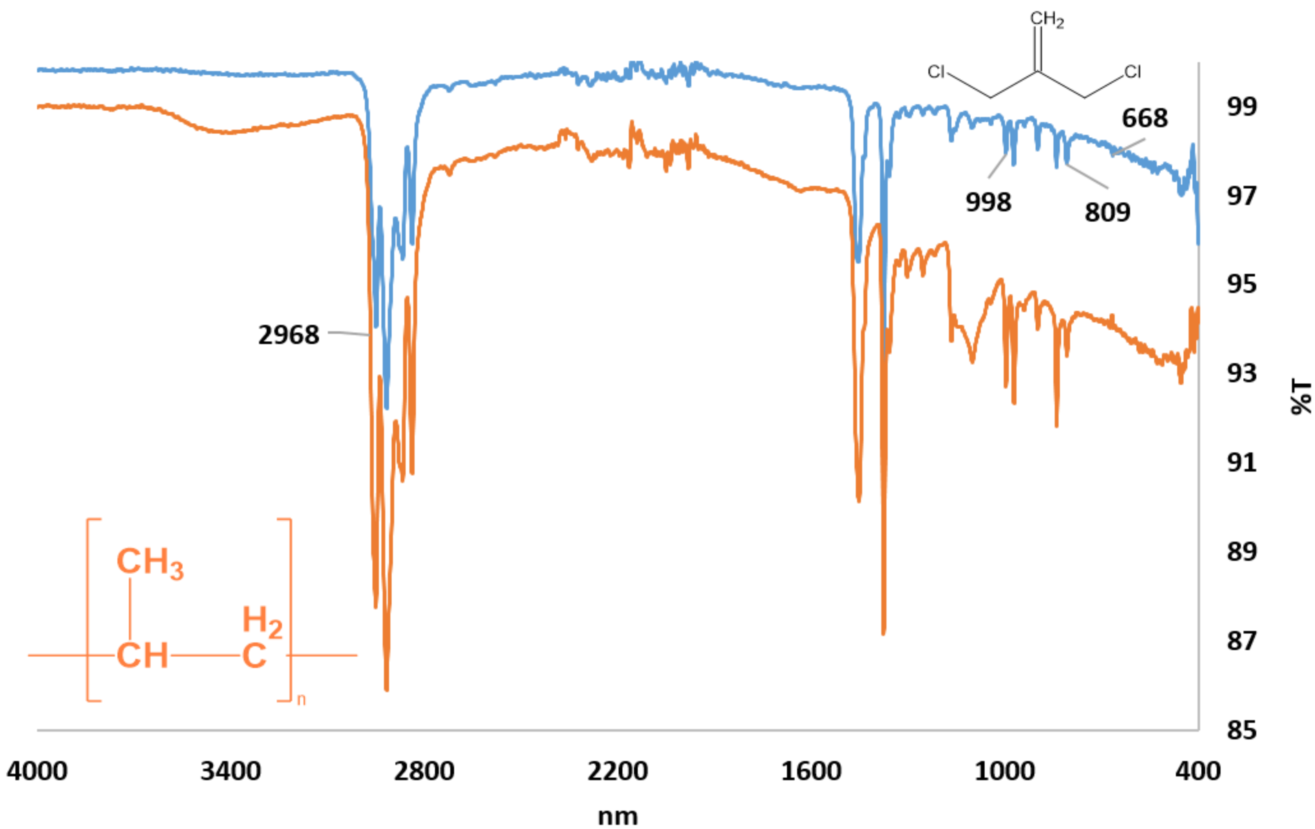

Figure 3. FT-IR graph of PP sample number 21 and PP fiber only

The orange peaks in the graph belong to untreated Polypropylene fibers, while the blue peaks belong to treated Polypropylene fibers. The 998cm^{-1} and 500cm^{-1} peaks in the fingerprint region are thought to belong to the C-H bonds of 3-Chloro-2-Chloromethyl-1-Propene. In addition, the 2968cm^{-1} peak is thought to belong to –CH_2 of 3-Chloro-2-Chloromethyl-1-Propene.

3.2. Fresh state properties

The amounts of water-reducing additives used in mortar mixtures and the spreading values of the mixtures are shown in Table 4. As can be seen from the table, adding PP fibers to the mixtures, regardless of the fiber type, increased the additive requirement for the target workability value [2]. In addition, increasing the fiber length further increased the additive requirement. The surface activation process on PP fibers showed different effects in mixtures containing 6 mm and 12 mm fibers. In 6 mm long PP fibers, the surface activation process slightly increased the admixture requirement compared to the untreated PP fiber mixture (6-PP) of the same length, while it did not change the additive requirement in mixtures containing 12 mm PP fibers.

Table 4. Spreading values of mortar mixtures and amounts of water reducing additives used

Mixtures	PCE requirement for target flow value (gr)	PCE ratio (%)	Flow value (cm)
Control	0.00	0.00	18.7
6-PP	0.75	0.15	18.0
M-6-PP	0.80	0.16	18.5
12-PP	1.00	0.20	18.6
M-12-PP	1.00	0.20	18.6

3.3. Flexural and Compressive Strengths

The 28-day flexural and compressive strength results of mortar mixtures are shown in Table 5. While the addition of 6 mm PP fiber to the mixtures decreased the flexural strength by 1%, the addition of 12 mm fiber increased it by 5%.

The flexural strength of mortar mixtures increased with the application of surface activation process to 6 mm long fibers. The opposite was observed with 12 mm fibers. It is thought that the surface activation process on the fibers slightly increased the adhesion between the matrix and the fiber. This situation may have increased the flexural strengths by reducing the tensile cracks formed as a result of bending [10]. However, it is thought that when 12 mm fibers are used in the mixtures, the negative effects are seen due to the fiber agglomeration in the mixture rather than the effect of the chemical surface activation process on the fibers.

No significant effect of PP fibers on the compressive strength was observed. It is thought that the compressive strengths decreased slightly due to some voids formed during the mixing.

Table 5. 28-day compressive strength results of mortar mixtures

Mixtures	Flexural Strength (MPa)	Compressive Strength (MPa)
C	7.72	40.60
6-PP	7.66	37.53
M-6-PP	7.81	37.92
12-PP	8.11	36.3
M-12-PP	8.02	37.2

4. Conclusion

The following results were obtained based on the analyses and experiments performed.

- Adding polypropylene fibers to mortar mixtures increased the need for water reducing additives for the target spreading value. Increasing the fiber length increased the need a little more.
- While the surface activation process on 6 mm long PP fibers slightly increased the workability of mortar mixtures, there was no significant change from 12 mm PP fibers.
- The surface activation process on PP fibers did not show a significant change on the spreading value of mortar mixtures.
- While the addition of 6 mm PP fibers to mortar mixtures increased the flexural strength, 12 mm fibers decreased the flexural strength. The surface activation process on 6 mm PP fibers increased the flexural strength of mortar mixtures.
- The surface activation process applied to PP fibers did not have a significant effect on the compressive strength.

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