Influences of molding processes and different dispersants on the dispersion of chopped carbon fibers in cement matrix

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Abstract

Chopped carbon fiber-reinforced cement composite (CFRC) has become one of the potential smart materials in recent years. The key process of preparing this kind of composite at the early stage is how to disperse carbon fibers evenly into the cement matrix to achieve CFRC composite with good properties. In this study, a three-step mixing process and a six-step mixing process for the preparation of CFRC were suggested, respectively. The fracture morphology was observed by scanning electron microscopy. The influence of mass fractions of three common dispersants methyl cellulose (MC), carboxymethyl cellulose sodium (CMC) and hydroxyethyl cellulose (HEC) on the dispersion of short carbon fibers in water under certain temperature was investigated prior to the manufacture of CFRC. The correlation between mass fraction and viscosity was discussed, and the dispersion effect was assessed from the structure of dispersants and molding process. A hypothetical capsule theory was proposed to reasonably explain the dispersion effect of MC, CMC, and HEC. The experiments showed that pre-dispersion by ultrasonic vibration improved the dispersion of carbon fibers greatly. The dispersivity of carbon fibers was closely related to the category and mass fractions of dispersants. With the same mass fraction of dispersants at a
certain temperature, the dispersion effect was in order of HEC > CMC > MC. Meanwhile, when the mass fraction of HEC was between 0.6 and 0.8 wt% by weight of cement and the mass fraction in the aqueous solution was between 1.65 and 1.80 wt%, carbon fibers dispersed most ideally and distributed further uniformly in the cement matrix.

Keywords: Mechanical engineering, Materials science

1. Introduction

Carbon fiber has high strength, high modulus, low density, excellent corrosion resistance and many other advantages [1, 2, 3, 4]. When it is added into the cement matrix, a carbon fiber-reinforced cementitious composite (CFRC) can be conveniently achieved [1, 5, 6, 7]. Compared with other kinds of fibers, carbon fibers can give CFRC characteristics of good tensile strength, bending strength, impact strength, and good explosion resistance as well as good electrical, thermal, and magnetic properties [8, 9].

Unfortunately, the surface of carbon fibers is hydrophobic and the weight is light, less than half of the cement specific gravity. The fiber diameter is much smaller than the cement particle. Consequently, it is difficult for carbon fibers to disperse uniformly in cement paste, which affects directly the mechanical, electrical and electromagnetic properties of CFRC composites [10, 11]. Good disperitivity of carbon fibers in the cement matrix is usually in favor of lower resistivity, higher flexural strength and toughness of the CFRC composites [12, 13]. In addition, a common blender will easily damage carbon fibers to reduce their strength. Therefore, how to distribute short carbon fibers evenly into the cement matrix is the key to prepare the CFRC composites of good performances [14, 15].

There are two steps for the dispersion of carbon fibers in CFRC. The first step is that carbon fibers are uniformly dispersed in the dispersant solution, and the second step is that the dispersive system of carbon fibers is evenly dispersed in the cement matrix. Both of the steps are actually a complex physical, chemical and mechanical processes [16, 17]. The mixing of the mixture, the agitation method, and the vibrating molding process all have a great influence on the dispersion of carbon fibers in the cement matrix and the density of the CFRC composites. The ramming molding process can effectively reduce the porosity in the composites and improve the strength. The viscosity of the dispersant system and the mixing process affect the dispersion of carbon fibers, too. The viscosity affects the dispersion of carbon fibers in the dispersant aqueous solution, while the viscosity and the mixing process affect their dispersion state in the cement matrix [1, 18, 19].
Researchers have tried different ways to improve the dispersion of carbon fibers in the cement paste, such as pre-treatment of carbon fibers and addition of dispersing agents [20, 21], which has become a hot topic of preparing CFRC composites with good properties [22, 23]. However, the usage of hydroxyethyl cellulose (HEC) to improve the dispersion of carbon fibers has been rarely reported. The improvement effect by methyl cellulose (MC), carboxymethyl cellulose sodium (CMC), and HEC is little compared in literatures. The influence of the combination of dispersants and molding processes on the dispersion degree of carbon fibers either in the aqueous solution or in the cement matrix is seldom investigated carefully.

With this in mind, in the present study, the surface lubrication effect of three kinds of dispersants MC, CMC, and HEC as well as the filling effect of silica fume was investigated in details. With the help of the colloidal theory and the surface adsorption theory, the influence of their mass fractions and viscosity on the dispersion degree of carbon fibers in the aqueous solution was compared from the chemical structure point of view of the three different dispersing agents. The three-step molding method and the six-step processing method were applied to assess the dispersive system of carbon fibers in the cement matrix. The macro-dispersion status of carbon fibers in the aqueous solution was observed by digital camera. The fracture morphology of the CFRC samples prepared by the three-step and six-step methods, respectively, was observed by scanning electron microscopy (SEM) to study the distribution of carbon fibers in the CFRC composites.

2. Experimental

2.1. Raw materials and main instruments

Dispersants used in this work were hydroxyethyl cellulose made in Shandong Yiteng Chemical Group Co., Ltd with the viscosity of 30000 Pa s, methyl cellulose made in Tianjin Fuchen Chemical Reagent Factory, and carboxymethyl cellulose sodium obtained from Xi’an Chemical Agent Factory. The specifications and quality indexes of carboxymethyl cellulose sodium are in accord with Q/09SRT009-2002 and the viscosity specifications can be adjusted between 10 and 5000 mPa s. Naphthalenesulfonate formal condensate (FDN) was used as a water reducer and it is a high efficiency water reducing agent made in Wuhan Iron and Steel Corporation Additive Factory. Liquid tributyl phosphate (TBP), made in Tianjin City Heng Hao Industry & Trade Co., Ltd, was used as a defoamer. All of them were chemically pure. Carbon fibers were polyacrylonitrile (PAN)-based chopped ones with the length of 6 mm obtained from Jilin Jiyan High-tech Fiber Co., Ltd.

Main instruments used were a LVTDV-Ⅰ typed Brookfield viscometer, a KQ-250DE typed numerical control ultrasonic unit made in Shanghai Kunshan Ultrasonic Instrument Co., Ltd, a J-160 typed cement paste mixer made in Wuxi Building...
Materials Manufacturing Equipment Factory, a WE-100B typed hydraulic universal testing machine made in Changchun, a SHBY-40B standard numerical control cement curing box, a HT-200 typed electronic balance, a M0110B electronic balance with the maximum range of 1100.00 g, and a JJ-5 typed cement mortar mixer made in Shenyang Dongwei Electric Machinery Manufacturing Co., Ltd.

2.2. Pre-dispersion of short carbon fibers

2.2.1. Dispersion of carbon fibers by ultrasonic oscillation in the aqueous solution

The weighed short carbon fibers were put into a 500 mL beaker. An appropriate amount of water was added into the beaker to make the carbon fibers fully immersed and the water was slightly excessive. The beaker was vibrated by the ultrasonic oscillation for 15 min, during which it can be observed that carbon fibers were driven to disperse by a large number of micro bubbles produced by microwave oscillation, and they tended to be in the status of monofilament. In the oscillating process, the intermittent mixing was done and the water temperature was kept between 38 and 44 °C. The ultrasonic power is 250 W.

2.2.2. Dispersion of carbon fibers in different dispersants

The dispersing agents were weighed in accordance with 0.6 wt% of the cement weight that was used for the subsequent preparation of CFRC composite samples. According to 0.5 wt% of the cement weight, FDN superplasticizer was weighed. Three 500 mL beakers with carbon fibers were prepared. The weighed dispersants of methyl cellulose, carboxymethyl cellulose sodium, and hydroxyethyl cellulose were, respectively, added into the beakers. Meanwhile, FDN water reducing agent was added into each beaker, stirring and continuously vibrating by ultrasonic oscillation for 10 min.

The mass fraction of the dispersant water solution was controlled between 1.65 and 1.80 wt%. The pH value of the water solution was equal to 7. If the mass fraction was too small, the viscosity of the dispersant was not enough to coat carbon fibers to form a so-called cysticercus capsule [24, 25]. If the mass fraction was too large, the viscosity of the solution was too greater and the fluidity was poor and carbon fibers can’t disperse separately. Therefore, it is important to control the mass fraction of the dispersing agents to promote the uniform dispersion of carbon fibers.

Under the same condition, the dispersion effects of MC, CMC and HEC on short carbon fibers were tested, respectively. It was found that the three dispersants all had good dispersion effects on short carbon fibers at different mass fractions. By comparison, much more bubbles appeared in the dispersive system when HEC dispersant was used, indicating that it is a better dispersing agent.
To eliminate micro air bubbles generated during ultrasonic oscillation, two drops of tributyl phosphate defoamer was added. After vibrating for 15 min, short carbon fibers were basically in single filament in the beakers. The aqueous solution system of carbon fibers was poured into a clean white enamel disk to observe the dispersion status. Fig. 1 shows two digital photos of the dispersion effect. Fig. 1(a) is the dispersion of carbon fibers when a small amount of dispersant was added and the vibration time was short, only 5 min by ultrasonic vibration. Obviously, the phenomenon of fiber clustering and aggregation is observed. When an appropriate amount of dispersant was added and the stirring and vibrating time was longer, approximately 15 min, carbon fibers were uniformly distributed as shown in Fig. 1(b).

The uniform dispersion of carbon fibers in the aqueous solution is the prerequisite to ensure their even dispersion in the cement matrix, which is the key step to prepare CFRC composites with good properties in the subsequent experiment.

3. Results and discussion

3.1. Influence of dispersant viscosity on the dispersion of carbon fibers

The viscosity of dispersant has an important influence on the dispersion of carbon fibers. It is closely related to the mass fraction of the dispersant and the temperature of the solution. In general, the mass fraction is proportional to the viscosity. The viscosity decreases with the increase of temperature.

Fig. 2 shows the curves of the viscosity of MC, CMC and HEC varying with the temperature at different mass fractions. It can be seen from Fig. 2(a) that, at the mass fraction of 0.4%, the viscosity of MC solution was almost not affected by temperature, while the viscosity of CMC and HEC decreased with the increasing temperature. Fig. 2(b) shows the influence of temperature on the viscosity when the mass fraction of dispersant was 0.8%.

![Fig. 1. Optical microscopy images of carbon fibers in the dispersant solution: (a) Poor dispersion; (b) Good dispersion.](https://doi.org/10.1016/j.heliyon.2018.e00868)
By comparing Fig. 2(a) with Fig. 2(b), it can be seen that the curves are very similar, indicating that the effect of temperature on the viscosity is similar. When the mass fractions of the dispersants were increased to 2%, the viscosity of MC solution almost remained still with the increasing of the temperature, the viscosity of CMC...
solution was slightly declined, and the viscosity of HEC solution was declined sharply as shown in Fig. 2(c).

By comprehensive analysis of Fig. 2(a), (b) and (c), it can be inferred that, under the same conditions, the viscosity of MC solution was the lowest and its temperature-viscosity curve was always at the bottom of the figure, the viscosity of CMC solution was next to that of MC and its temperature-viscosity curve was in the middle, and the viscosity of HEC solution was the largest and its temperature-viscosity curve was always located on the top. In other words, the viscosity ranges from large to small in the order of HEC > CMC > MC.

When the mass fraction was fixed, the viscosity of the dispersant solution was reduced with the increase of temperature. When the temperature was certain, the viscosity was increased with the increase of the concentration of the solution.

The viscosity of the HEC solution varies greatly with the temperature, which is mainly due to the change of the cellulose chain structure. Fig. 3 shows the viscosity

![Fig. 3. Curve of viscosity variation in HEC aqueous solution: (a) varying with mass fraction; (b) varying with ultrasonic time.](image-url)
of HEC solution varies with the mass fraction shown in Fig. 3(a) and with the oscillation time shown in Fig. 3(b) at the temperature of 25 °C. In Fig. 3(a), the viscosity of HEC solution increases with the mass fraction, but not linearly. This phenomenon shows the intertwined reaction with each other may take place between a small number of side chains of the HEC main chain besides the interaction between the main chains of HEC molecules. HEC aqueous solution is a shear thinning non-Newtonian fluid with the characteristic viscosity of 0.9488 [15, 26, 27]. The viscosity is reduced in the aqueous solution due to the action of water molecule on the HEC molecular chain. Under the action of no shear force, the viscosity of HEC decreases with time, mainly due to the degradation of enzymes in the environment and the aging caused by the presence of polyelectrolyte in the solution [7, 28, 29].

Fig. 3(b) shows the viscosity of HEC aqueous solution varies with time. At the initial stage before 8 h, the viscosity decreased sharply with time. Between 10 and 45 h, the curve slowed down slightly. From 45 to 50 h, the curve swooped down suddenly. After 50 h, the curve in general tended to slow down gently. This is because in the early dissolution of HEC, the solvent water molecule penetrated into the HEC molecular chains and the interaction occurred between the water molecules and HEC molecular chains to weaken the interaction between HEC chains.

There is a huge volume gap between HEC molecules and water molecules. The HEC molecules move slowly, so the dissolution rate is slow. With the lapse of time, the HEC chain surrounded by water molecules moves acceleratedly. The acting force between the water molecules and the HEC molecules is greater than that between the HEC molecular chains, resulting in the increasing distance between the HEC molecular chains. As a result, the force between the HEC molecular chains is reduced and the viscosity decreases sharply. When the force between the water molecules and the HEC molecular chain balances with the force between the HEC chains, the viscosity is also stable at the same time.

It can also be seen from Fig. 3(b) that the viscosity of the HEC solution system decreases slightly again from 50 to 125 h, which is due to the entanglement and interaction between a small number of side chains on the HEC molecular chain. As time goes on, this entanglement is destroyed by the water molecules that surround the HEC molecular chains, which further weakens the interaction between the HEC chains. Therefore, the viscosity further decreases, but the decline tends to be gentle.

3.2. Effect of silica fume filling on the dispersion of carbon fibers in the cement matrix

Silicon powder particles are very thin. The average particle size is 0.1 μm, 100 times smaller than the diameter of Portland cement particles. The specific surface area of silica fume is between 15000 and 20000 m²/kg, containing 85—90% of the active
silica [7, 15, 30]. After mixing with cement, silicon powder can react quickly with calcium hydroxide to form hydrated calcium silicate and produce the strength.

The strength of silica fume doped cement after 28 days is higher than that of the base cement. The strength generated by one hundred grams of silica fume is equivalent to the strength produced by 200—500 grams of cement [15, 31].

Another feature of silica fume is its smaller fineness. Its specific surface area is 4—5 times that of the fly ash. Its activity is very high and it can adsorb more water reducers, air entraining agents and other admixtures. Thus, a large amount of water is required. Therefore, a high efficiency water reducing agent should be added together with silica fume to reduce the water consumption of cement. In addition, the cohesiveness of cement is increased with the increasing amount of silica fume. At this movement, the phenomenon of bleeding or segregation of concrete is not likely to happen, but the excessive cohesion influences the concrete pumping of the construction workability and produces shrinkage cracks easily. Moreover, silica fume is more expensive, so its additive amount is usually controlled between 5 and 10%.

In this work, 12 wt % of silica powder by weight of cement was added into the cement matrix to improve the dispersion of carbon fibers [7, 32] and to enhance the interfacial bonding force between carbon fibers and the cement matrix. Major parameters of silica fume are shown in Tables 1 and 2, respectively. From Table 1, it can be seen that the main component of silica fume is SiO$_2$, accounting for 95.15% and other chemical components are 1.26% Al$_2$O$_3$, 0.66% SO$_3$, 0.43% MgO, 0.36% CaO, and 0.23% Fe$_2$O$_3$. From Table 2, it can be seen that the particle size of silica fume is very small, while the specific surface area is large. Therefore, silica fume has a very good filling effect. Due to the particle effect and the absorption effect, it can not only fill the gaps between cement particles, but can seep into the gaps between carbon fibers to separate them to improve their dispersion [1, 7, 15]. At the same time, it can be well distributed on the surface of cement and carbon fibers to improve the interface between cement and fibers to eventually increase the bonding degree of the interface.

### Table 1. Major chemical components of silica fume.

| Component | SiO$_2$ (%) | Fe$_2$O$_3$ (%) | Al$_2$O$_3$ (%) | MgO (%) | CaO (%) | SO$_3$ (%) |
|-----------|-------------|-----------------|-----------------|---------|---------|-----------|
| SiO$_2$   | 95.15       | 0.23            | 1.26            | 0.43    | 0.36    | 0.66      |

### Table 2. Index of silica fume.

| Property                 | Stacking density (kg/m$^3$) | Specific surface area (m$^2$/kg) | Average particle size (µm) | Loss on ignition (%) | Water demand (%) |
|--------------------------|-----------------------------|----------------------------------|---------------------------|----------------------|-----------------|
| Stacking density (kg/m$^3$) | 200 ~ 300                   | 15000 ~ 20000                    | 0.1                       | 2.15                 | 136             |
Silicon powder can effectively reduce the electrical resistivity of carbon fiber-reinforced conductive concrete and increase the compressive strength and the flexural strength [1, 15]. By the synergistic dispersion of a dispersant and silica powder with a suitable mixing process, CFRC composites with good properties can be prepared.

When HEC and silicon powder are added into the mixture, the viscosity increases with the increase of the mass fractions of HEC and silicon powder. As described previously, the dispersion of carbon fibers in CFRC includes two steps: the first step is the dispersion of carbon fibers in the dispersant aqueous solution and the second step is in the cement matrix. In both processes, the viscosity of the dispersant plays a positive role.

On the one hand, the viscosity changes the rheological properties of the carbon fiber suspension and makes the suspension have a low-Reynolds number [15, 23]. In other words, the flowage proceeds in order and the movement of carbon fibers increases with the fluid. Thus, the freedom of the motion of carbon fibers in water is greatly limited, reducing the possible flocculation caused by the interaction between the fibers and the collision between them. With the increase of the suspension viscosity and the enhance of the steric hindrance of the dispersant, the suspension property of carbon fibers in the medium is increased and the time of fiber sedimentation and re-flocculation is prolonged, which is conducive to the uniform dispersion of carbon fibers.

On the other hand, the higher consistency is beneficial to the dispersion of carbon fibers in the cement matrix during the final mixing of CFRC.

### 3.3. Influence of the three-step mixing process on the dispersion of carbon fibers

The mixing process is very important in the preparation of CFRC composites. Different mixing processes exert different influences on the dispersion of carbon fibers in addition to the choice of the dispersants. Usually, the mixing processes are divided into three steps as shown in Fig. 4, which include (a), (b), and (c) flow charts. By the three-step technique in Fig. 4(a), water and cementitious materials are firstly mixed uniformly. Then, carbon fibers are added into the mixture to achieve the finished CFRC product. By the three-step technique in Fig. 4(b), carbon fibers and cementitious materials are firstly mixed and then moderate amount of water is added to stir continuously for 2 min to obtain the finished CFRC composites. By the three-step technique in Fig. 4(c), water and carbon fibers are firstly mixed and then cementitious materials are added to stir continuously for 2 min to achieve the finished CFRC composites. In each process, three steps are involved, hence the name of three-step technology.
To compare the effect of different mixing processes, two SEM images of each process are displayed in Figs. 5, 6 and 7, respectively, when the mass fraction of carbon fibers is 0.8 wt% by weight of cement.

By experiments, it is known that the resistivity and the strength of the CFRC test block made by the three-step technique in Fig. 4(a) exhibits the largest dispersion degree (1, 7, 15). The phenomenon of a large number of fibers agglomeration is observed in the test blocks as shown in Fig. 5(a) and (b). Clearly, carbon fibers exist in fascicule and there are clearances in the cement matrix. The composites is not compact and the mechanical strength is poor.

By the three-step technique in Fig. 4(b), the dispersion degree of the electrical resistivity and the strength of CFRC is slightly larger [21, 26]. No obvious fibrous cluster

Fig. 4. Flow charts of the three-step mixing technology (a), (b) and (c) for the preparation of CFRC.
was found in the crushed specimen, indicating that carbon fibers are almost uniformly distributed. The SEM images of the fracture surface of the samples are shown in Fig. 6(a) and (b).

By the three-step technique in Fig. 4(c), the dispersion degree of the electrical resistivity and the strength of the CFRC composites are the largest [5, 13]. Still, no obvious fibrous cluster was found in the crushed specimen and the dispersion of carbon fibers was more uniform. The SEM images of the fracture surface of the CFRC composites are shown in Fig. 7(a) and (b). Relatively, carbon fibers are almost distributed uniformly in the cement matrix.
There are reasons for the appearance of the phenomena above. By the three-step technique in Fig. 4(a), the cementitious materials are initially mixed and stirred, and then carbon fibers are added. Due to the hydrophobicity of carbon fibers, it is not easy for bundles of carbon fibers to disperse uniformly. As a result, carbon fibers are in the status of fascicles. By the three-step technique in Fig. 4(b), the cementing materials and fibers are firstly mixed and stirred, in the process of which cement and silica fume particles can easily penetrate the gaps between carbon fibers, especially smaller silica powder. Under such a circumstance, carbon fibers are almost evenly distributed prior to the addition of water. By the three-step technique in Fig. 4(c), carbon fibers are firstly added into water. Under this condition, there are two cases: when a large number of carbon fibers are added, they can’t be well infiltrated owing to insufficient water; when a small number of carbon fibers are added, they can be soaked completely in the aqueous solution and the dispersant can play its full role in the dispersion. Eventually, carbon fibers are well distributed.

3.4. Influence of the six-step molding process on the dispersion of carbon fibers

In addition to the three-step technique for the dispersion of carbon fibers, we also developed the six-step molding method. The flow chart is shown in Fig. 8. The entire mixing process of the mixture is actually in an order of wet → wet-dry → wet process. Firstly, 50 grams of carbon fibers were placed in a 500 mL beaker and 3/5 of the total amount of water used in the experiment was added into the beaker. The beaker was vibrated by the ultrasonic oscillation for 15 min. During the process, a large number of micro bubbles were generated which drive carbon fibers to separate in the solution. This process is reversible. When the ultrasonic oscillation is stopped, the fibers intend to gather together. Therefore, the beaker must be vibrated continuously. HEC dispersant was added and the beaker was vibrated for another 10 min. At this moment, carbon fibers were in single state in the sticky dispersed system. Silica fume, FDN superplasticizer, and 3/5 of the total amount of cement used in this study were then added into the beaker, stirring manually by a glass rod for a while. This mixture was poured into an agitator and stirred for another 2 min. This is the wet mixing process during which free water decreased.

The mixing of the cement added subsequently with the mixture formed previously is a dry-wet mixing process. It is not a dry mixing and wet mixing in general sense. At this time, there is some free water but poor mobility, so this mixing process is called the dry-wet mixing. At this stage, the cement particles are blended with carbon fibers through the forced action of the blender blades. Some of the fibers may be broken. Finally, the remaining 2/5 of water was added to improve the fluidity of slurry during the mixing process. This is a process similar to a wet mix. By this process, the workability of cement paste can be effectively improved and the consistency of mixture
can be reduced. The ability of mutual diffusion between cement particles and fibers is enhanced to achieve the homogenization system consisting of carbon fibers, water, and cement particles.

Therefore, the mixing process of wet-mixing → dry-wet mixing → wet mixing is conducive to the dispersion of carbon fibers in the cement matrix. In the two processes of carbon fiber dispersion, the surface lubricating of the HEC dispersant, the increase of the dispersant viscosity, and the filling effect of ultrafine silicon powder particles improved the dispersion of carbon fibers in the interior of the dispersant solution. And the high viscosity and the forced mixing process made carbon fibers uniformly dispersed in the cement matrix.

Additionally, the vibration forming process also has a great influence on the density of the samples. Fig. 9(a) and (b) show the density of the specimen after vibration only once. There are more pores and larger distances between the fibers. It is predicted that the mechanical properties of the specimen will be poor. The prepared CFRC can’t meet the needs of actual engineering.

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**Fig. 8.** Flow chart of the six-step mixing technology in the preparation of CFRC.
Fig. 9(c) and (d) show the SEM morphologies of the fracture of the CFRC test pieces after vibrating three times on a platform vibrator, vibrating 60 s each time, automatically controlled. Comparatively, carbon fibers are evenly distributed and the density of the samples looks compact.

3.5. Influence of the cellulose structure on the carbon fiber dispersion

As mentioned previously, three kinds of cellulose dispersants MC, CMC and HEC all have good dispersing effects on carbon fibers in the aqueous solution.

One of the important reasons why carbon fibers are difficult to disperse in the cement paste is the hydrophobicity of carbon fiber surface. Adding a surfactant is an important way to improve the surface hydrophobicity of carbon fibers. Methyl cellulose and carboxymethyl cellulose are surface active agents and they can promote the dispersion of carbon fibers in the cement paste. When they are added into water, they can better wet the surface of carbon fibers and make them homogeneously dispersed in monofilament. Meanwhile, a sticky thin layer of film can be formed on the fiber surface to prevent fasciculation of dispersed fibers.

Methyl cellulose decreases the surface tension of the fibers as well as the surface energy of the cement matrix. Therefore, a large number of air bubbles will be introduced into the cement paste in the mixing process. In addition, the methyl cellulose aqueous solution belongs to an expansion fluid and its addition will also lead to the increase of the viscosity of cement paste. With the increase of its dosage, this effect is more and more obvious. To make full use of its dispersibility to improve...
the workability of the mixture and reduce the number of bubbles, tributyl phosphate is usually added as a defoamer, and naphthalene sulfonate formaldehyde condensate, a water reducing agent, is added as well [7, 15].

There are polar carbonyl groups and hydroxyl groups on the carbon fiber surface. Intermolecular hydrogen bonds can be formed between the two groups and water molecules. Consequently, the carbon fiber surface has, to some extent, hydrophilicity and wettability in the aqueous solution. In other words, carbon fibers exhibit dispersibility. Methyl cellulose, carboxymethyl cellulose, and hydroxyethyl cellulose all belong to polymer compounds. They all contain longer cellulose chains in their unit structures as shown in Fig. 10. Fig. 10(a) is the structural unit of methyl cellulose, (b) is the structural unit of sodium carboxymethyl cellulose, and (c) is the structural unit of hydroxyethyl cellulose.

The longer the cellulose chain, the greater the viscosity. The viscosity reflects the interaction between the molecules. The factors that affect the viscosity include the mass fraction of the solvent, the temperature at the time of measurement, and the type of the viscosimeter used. The changes of mass fraction or temperature can change the final viscosity of the solution.

Methyl cellulose is a kind of non-ionic water-soluble polymer. Sodium carboxymethyl cellulose is a water-soluble cellulose ether, an anionic surfactant. Hydroxyethyl cellulose is a kind of non-ionic soluble cellulose ether, a nonionic surfactant, and it is a water-soluble polymer compound.

Fig. 10. Unit structures of dispersants: (a) Methyl cellulose (MC), (b) Carboxymethyl cellulose (CMC), and (c) Hydroxyethyl cellulose (HEC).
By analysis of the structural units of cellulose in Fig. 10(a), (b), and (c), it can be found that each cellulosic unit contains a stable six-membered ring and polar hydroxyl group -OH. Hydrogen bonds can be formed between the polar hydroxyl group, the polar hydroxyl or carbonyl group on the carbon fiber surface, and the polar water molecules. The formation of hydrogen bonds and the interaction between molecules increase the hydrophilicity and wettability of carbon fibers as well as the cohesive force between carbon fibers, water, and the dispersants. In addition, an appropriate external force, i.e. ultrasonic oscillation and mixing, is coupled. Eventually, carbon fibers are uniformly dispersed in the aqueous solution, forming a colloidal dispersion system.

Comparatively speaking, hydroxyethyl cellulose contains more polar groups in its structure. Therefore, more hydrogen bonds can be formed between the polar groups and carbon fibers, which endow carbon fibers with stronger hydrophilicity and wettability. As a result, the dispersion effect is the best.

In addition, when methyl cellulose and carboxymethyl cellulose are used as dispersants in the solution containing inorganic salts, their viscosity will decrease. However, when hydroxyethyl cellulose is used as a dispersant in the solution of inorganic salts, its viscosity is hardly affected by inorganic salts [6, 7, 15]. Therefore, it can be said that hydroxyethyl cellulose is the most ideal dispersant of the three.

### 3.6. Distribution of major elements and hypothetical capsule theory

#### 3.6.1. Distribution of major elements in the cement paste and in CFRC

To further investigate the variation of major elements Ca, O, Si, and C in the cement matrix after cement was made into CFRC composites, a SEM image of cement paste and the corresponding Energy Dispersion Spectrum (EDS) are provided in Fig. 11. It can be seen from the left-hand ESP spectrum that Ca element exhibits the highest peaks, next are in sequence of O, Si and C elements.
For quantitative analysis, the distribution of four major elements Ca, O, C, and Si is provided in Table 3. By weight percentage, the content of the four elements are in order of Ca, O, C, and Si, and they are 49.93%, 41.67%, 6.41%, and 1.98%. But by atomic percentage, they are in order of O, Ca, C, and Si and they are 58.47%, 27.96%, 11.98%, and 1.59%. Obviously, the sequence of Ca and O is changed.

Fig. 12 provides a SEM image of CFRC when carbon fibers were distributed appropriately in the cement matrix. The corresponding EDS spectrum is shown in the right hand. It can be seen the peaks of elements of Ca, Si, and O are relatively apparent. In addition, peaks of other elements such as Fe, Al, and S are also observed. This is because lots of substances were added into cement in the preparation of CFRC.

For quantitative comparison, Table 4 provides the weight and atomic percentage of the four major elements and other elements. Clearly, by weight percentage, the content of four major elements from large to small is in order of Ca, O, Si, and C. They are in proper sequence of 49.20%, 32.48%, 10.50%, and 2.98%. The corresponding atomic percentages are 30.57%, 50.54%, 9.31%, and 6.18%, respectively.

For clear comparison, the variation of major elements of Ca, O, Si, and C before cement paste was made into CFRC and after it was prepared to CFRC is listed in Table 5. From Table 5, it can be seen, by weight percentage, element Si varied by 64.0%, the highest value. Next are the element C by 51.0%, O by 22.0%, and Ca by 1.0%. By the atomic percentage, element C varied greatly by 289%, the maximum value. Next are Si by 22.0%, O by 14.0%, and Ca by 9.0%.

Table 3. Elements in standard cement paste (Cement/sand/water = 1:3:0.5).

| Element | Weight% | Atomic% | Remarks |
|---------|---------|---------|---------|
| Ca K    | 49.93   | 27.96   |         |
| O K     | 41.67   | 58.47   |         |
| C K     | 6.41    | 11.98   |         |
| Si K    | 1.98    | 1.59    |         |
| Total   | 100.00  |         |         |

Fig. 12. SEM image and EDS spectrum of CFRC sample with carbon fiber content of 0.8 wt% by weight of cement.
There are three kinds of theories about the dispersion of solid substances in aqueous solution: the theory of wetting, the theory of electric double layer and the theory of colloid protection [4, 9, 15]. To better understand the dispersion effects of the three dispersants of MC, CMC and HEC, a “capsule” theory is assumed.

The three dispersants of MC, CMC and HEC are all surfactants. They all contain hydrophilic groups -OH, hydrophobic groups -R, glucose-like structural units in their structures. At a given temperature, they have good dispersing effects on short carbon fibers. The main difference is that the molecular chain structure and the length of the non-polar groups in the three dispersant structures are different.

Hydrogen bonds can be formed between the polar hydrophilic groups of the surfactants and the polar groups on the carbon fiber surface or van Edward force interacts with each other. Thus, the dispersant is acted as a water-soluble lubricant to form a thin layer of lubricating film on the fiber surface. Carbon fibers are wrapped. As a result, numerous of “capsules” are formed to constitute a so-called colloidal dispersion, in which each carbon fiber behaves like a colloidal particle. Attraction and

**Table 4.** Element contents in CFRC with carbon fiber content of 0.8 wt% by weight of cement.

| Element | Weight% | Atomic% | Remarks |
|---------|---------|---------|---------|
| Ca K    | 49.20   | 30.57   |         |
| O K     | 32.48   | 50.54   |         |
| Si K    | 10.50   | 9.31    |         |
| C K     | 2.98    | 6.18    |         |
| Al K    | 1.47    | 1.36    |         |
| S K     | 1.38    | 1.07    |         |
| Fe K    | 1.54    | 0.69    |         |
| K K     | 0.45    | 0.28    |         |
| Total   | 100.00  |         |         |

**Table 5.** Comparison of major elements in cement paste and in CFRC.

| Element | Weight% Cement paste | Weight% CFRC | Difference | Variation (%) Cement paste | Difference | Variation (%) CFRC | Remarks |
|---------|----------------------|--------------|------------|-----------------------------|------------|---------------------|---------|
| Ca K    | 49.93                | 49.20        | 0.73       | 1.0%                        | 27.96      | 30.57               | 27.96   |
| O K     | 41.67                | 32.48        | 9.19       | 22.0%                       | 58.47      | 50.54               | 7.93    |
| Si K    | 6.41                 | 10.50        | -4.09      | 64.0%                       | 11.98      | 9.31                | 2.67    |
| C K     | 1.98                 | 2.98         | -1.00      | 51.0%                       | 1.59       | 6.18                | -4.59   |

**3.6.2. Hypothetical capsule theory**

There are three kinds of theories about the dispersion of solid substances in aqueous solution: the theory of wetting, the theory of electric double layer and the theory of colloid protection [4, 9, 15]. To better understand the dispersion effects of the three dispersants of MC, CMC and HEC, a “capsule” theory is assumed.

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Hydrogen bonds can be formed between the polar hydrophilic groups of the surfactants and the polar groups on the carbon fiber surface or van Edward force interacts with each other. Thus, the dispersant is acted as a water-soluble lubricant to form a thin layer of lubricating film on the fiber surface. Carbon fibers are wrapped. As a result, numerous of “capsules” are formed to constitute a so-called colloidal dispersion, in which each carbon fiber behaves like a colloidal particle. Attraction and
repulsion exist between the colloidal particles. When the dynamic equilibrium is established between them, a certain distance maintains between the particles, forming a relatively stable colloid dispersion system [10, 14]. Carbon fibers are no longer entangled together and they tend to be monofilament [13, 15].

When the quasi colloidal dispersion system is formed, a positive adsorption is generated at the solid-liquid interface, and the surfactant concentration increases at the interface [7, 15]. The “capsules” are floating in the dispersion system. Carbon fibers present a good dispersion state. According to the Gibbs formula (1), there is positive relationship between the surface tension and the amount of substance:

\[
\Gamma = -\frac{C}{RT} \frac{d\sigma}{dC}
\]

where \(\Gamma\) refers to the surface adsorption capacity, \(\text{mol/cm}^2\); \(C\) is the amount of substance concentration, \(\text{mol/L}\); \(\sigma\) stands for the surface energy, \(10^{-3}\ \text{N/m}\); \(T\) is the absolute temperature, \(\text{K}\); \(R\) means the universal gas constant; \(\frac{d\sigma}{dC}\) represents the change rate of the surface tension, indicating the size of the surface activity of the substance.

According to formula (1), the surface energy \(\sigma\) is proportional to the amount of substance, namely, the mass fraction \(C\). When the mass fraction of the dispersant is too small, the viscosity of the solution is low and carbon fibers can not be surrounded by sufficient polar groups to form “capsules”. When the mass fraction increases properly, the free energy is reduced, the thermodynamic stability of the system increases and the whole dispersed system tends to be stable. In this case, carbon fibers are in good dispersive state. However, when the mass fraction is too large, an excessive viscosity appears which affects the fluidity of the dispersion system. The dispersion of carbon fibers are hindered.

In this study, only when the mass fraction of the dispersant is controlled between 1.66 and 1.80%, the viscosity produced by the dispersant can make numerous “carbon fiber capsules” formed in the dispersion system. Carbon fibers can be dispersed evenly in the colloidal dispersion system.

Additionally, the addition of the three kinds of dispersants MC, CMC and HEC reduces the surface tension of the liquid. Therefore, there is a great foaming force in the dispersion system. The bubbles produced can make carbon fibers keep distance from each other, avoid the contact between fibers, prevent the fibers from curling and bending, and eventually prevent the adhesion and cluster formation between fibers. Meanwhile, when the carbon fiber dispersion system mixes with the cement matrix, the dispersants are adsorbed on the surface of cement particles, forming a glue lubrication layer which prevents the formation of cement flocculation structure [1, 7, 15].

Compared with MC and CMC, HEC is a kind of water-soluble polymer [7, 15]. There are more hydroxyl polar groups in HEC structure, so it has strong...
hydrophilicity and is easy to dissolve in water. Hydrogen bonds or bridging is likely to be formed between the polar groups in the carbon fiber surface and hydrogen and oxygen atoms in water. Therefore, it has a better dispersion effect.

4. Conclusions

The influences of the three-step and six-step molding processes as well as different dispersants on the dispersion of carbon fibers in CFRC were investigated. The structure of the dispersants of MC, CMC, and HEC were analyzed. Major conclusions drawn are as follows:

1. The dispersion of carbon fibers in CFRC includes two processes: firstly in the aqueous solution and then in the cement matrix. When the mass fraction of the dispersant was between 1.65 and 1.80% in the aqueous solution, the so-called capsules may be formed inside which carbon fibers were enclosed by the viscous dispersant solution, floating in the system. There are both attractive force and repulsive force between the capsules. When the two forces reach equilibrium, a relatively stable dynamic colloidal dispersion system is formed in which carbon fibers are in the status of good dispersion.

2. The mixing process exerted great influences on the dispersion of carbon fibers. The three-step molding process and the six-step molding process have their own advantages and disadvantages. When the mass fraction of carbon fibers is less than 1.2%, the three-step mixing technology prevails; when more than 1.2%, the six-step mixing technique is applied. For any mass fractions of carbon fibers, the appropriate mixing process is the six-step technology which can be summarized as wet-mixing → dry-wet-mixing → wet-mixing.

3. When the water/cement ratio is 0.44, the content of silica fume is 10%, the amount of water reducer is 1.3%, the volume fraction of the defoaming agent is 0.05%, the mass fraction of HEC is 0.6–0.8% by weight of cement and the mass fraction of the HEC aqueous solution is 1.65–1.80%, carbon fibers exhibit the optimal dispersion state in the aqueous solution.

4. MC, CMC, and HEC all contain polar hydroxyl groups. Hydrogen bonds can be formed between the hydroxyl groups, the polar hydroxyl groups or carbonyl groups on the surface of carbon fibers, and water molecules, enhancing hydrophilicity and wettability of the carbon fiber surface to further improve the dispersion of carbon fibers. Of the three dispersants, HEC contains more hydroxyl polar groups in its structure and it is more easily to be dissolved in water to form hydrogen bonds or to bridge with polar groups on the surface of carbon fibers to eventually improve the dispersion of carbon fibers. Under a certain temperature, three dispersants all have good dispersion effects on carbon fibers at different mass fractions. Under the same mass fraction, the dispersing effect
is in the order of: HEC > CMC > MC, that is, HEC has the best dispersion
effect on carbon fibers. Although HEC is conducive to the dispersion of carbon
fibers, an excess amount of it is unfavorable to the dispersion because this
sticky substance will increase the consistency of the cement.

Declarations

Author contribution statement

Wang Chuang, Peng Lei, Li Bing-Liang, Gao Ni, Zhao Li-ping, Li Ke-Zhi: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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