

The Influence of Fatty Alcohol Ether Phosphate Salt on Carbon Fiber's Dispersion Property

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ABSTRACT: The influence of fatty alcohol ether phosphate salt on the dispersion property of carbon fiber in oil material is assessed by the settling time, the turbidity and the dispersant condition of carbon fiber in oil material, and the surface morphologic structure and chemical composition of carbon fiber before and after leaching silk are characterized by field emission scanning electron microscope, scanning tunneling microscope, and X-ray photoelectron spectroscopy. Experiments show that fatty alcohol ether phosphate salt can improve the dispersion of carbon fiber in oil material significantly, and the optimum leaching silk concentration of fatty alcohol ether phosphate salt is 0.3%, while dispersants would spread over on the surface of carbon fiber evenly and the maximum turbidity value and the longest settlement time is 1.081 NTU and 28 min, respectively. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41470.

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INTRODUCTION

Carbon fiber (CF) is a specialty fiber and more than 90% of its chemical composition is carbon element.^{1,2} Carbon fiber has good electrical properties, thermal properties and mechanical property, so it has been used as structural or functional material in the field of aerospace, aviation, sports, architecture, etc.³ Carbon fiber can not only be used alone but also be made into composite materials, but the vast majority of carbon fiber is in the form of composite materials, such as carbon fiber reinforced cement-based composite materials (CFRC), carbon fiber-reinforced resin composite material (CFRP), etc. However, carbon fiber reinforced resin matrix composites have the most widely application scope. In the process of preparation, considering the high price of the carbon fiber, we should try to make the carbon fiber disperse in the matrix evenly to exert the reinforcing effects of carbon fiber effectively without increasing the amount of carbon fibers to improve the mechanical properties and smart features of composite materials, significantly.^{3–5}

However, carbon fiber dispersion has been a problem during preparing composite materials. The main reasons for the poor dispersion of carbon fiber in the matrix are:⁶ (1) Carbon fiber has turbostratic graphite structure and adjacent carbon atoms are connected with nonpolar covalent bonds, so the surface of carbon fiber has fewer active groups and low surface activity;

(2) Carbon fiber is easy to agglomerate and not easy to disperse in the matrix for its tiny monofilament and large surface area; (3) Some impurities are adsorbed on the surface of carbon fiber when it is out of the carbonization furnaces or in the processing and transportation, which reinforces the adhesive force between the fibers and affects its dispersing property. So we should consider adding dispersant treatment or starting from the fiber itself to improve the dispersion of carbon fibers in the matrix. In recent years, more and more domestic and international scholars have focused on the study of carbon fiber dispersion in the matrix. The study of the dispersion of carbon fiber in the oil materials is rare compared with in aqueous matrix.^{7–11} The research on the dispersion of carbon fibers in oil materials is the key to transient process for the dispersion study of carbon fiber in the resin matrix, and it also lays a stable foundation for the future dispersion research of carbon fiber in the other oil substrate material.¹² The traditional dispersion method is to put carboxymethylcellulose (CMC) and polyacrylamide into matrix directly, which led to the matrix spreading out on the carbon fiber surface.^{1,5,10} By this dispersant method, matrix can replace dispersion to spread on the surface of carbon fiber and affect dispersion performances. Moreover, matrix with dispersant can have an effect on composite material strength. To solve these problems mentioned above, we break the conventional dispersion methods and choose dispersant MLBH seldom used in the

Table I. Major Parameters of Carbon Fiber

Types (K)	Diameter (μm)	Density ($\text{g}\cdot\text{cm}^{-3}$)	Strength (GPa)	Modulus (GPa)	Elongation at break (%)
3	7	1.76-1.78	2.5-3.0	200-220	1.25-1.50

carbon fiber dispersion study. In this article, to explore the dispersion of carbon fiber in oil materials we first pretreat the wire, then leach the wire and finally disperse using MLBH as dispersants.

Fatty alcohol ether phosphate salt (MLBH) is a kind of anionic surfactant which features good dispersion and adhesion. It would hold two kinds of different materials properties together by the “molecular bridge” between carbon fiber and oily substrate interface when MLBH evenly spread out on the surface of carbon fiber, thus enhancing the mechanical properties of the materials and increasing the bonding strength. The main dispersing mechanism for the dispersion of carbon fiber in the matrix were:^{1,12} (1) Adsorbed on the surface of carbon fibers by adhesion, it is equivalent to spreading a thin layer of lubricating film on the surface of carbon fiber and the friction or adhesion between the fibers is reduced, making the fibers slide each other easily with less tangles; (2) The surface charge increased with increasing the repulsive force between the fibers, which can achieve good dispersion.

The experiment selects polyacrylonitrile (PAN)—based carbon fiber which is more difficult to disperse and the sedimentation time, the turbidity value and the decentralized state are the evaluation methods to analysis the influence of the dispersion of MLBH on carbon fiber in the oily materials, so the optimal dispersion conditions of carbon fiber in the oily materials can be determined.

EXPERIMENTAL

Materials

PAN-based carbon fiber was purchased from Jiyan High-tech Co., LTD. (Jilin, China), and its major parameters are shown in Table I; Acetone ($\text{C}_3\text{H}_6\text{O}$) was analytical reagent and obtained from Tianjin North Tianyi Chemical Reagent Factory; Dispersant MLBH was technical grade and purchased from Tianjin Polytechnic University Textile Auxiliaries Co., LTD; Solvent naphtha S60n was technical grade and purchased from Tianjin Polytechnic University Textile Auxiliaries Co., LTD; Analytic balance (FA2004N) was purchased from Shanghai Jinghai Equipment Co., LTD; Field emission scanning electron microscope (S-4800) was purchased from Japan Hitachi Limited; Scanning tunneling microscope (STM.IPC-250) was purchased from Chongqing University; X-ray photoelectron spectroscopy (K-Aepna) was purchased from America ThermoFisher Company; and Turbidity meter (2100AN) was purchased from America HACH Company.

Methods

Pretreatment of Carbon Fiber. To remove organic impurities and pigment on the surface of the carbon fibers, we put appro-

prate amount of carbon fiber in Soxhlet extractor filled with acetone for 2 h, then wash the carbon fibers with distilled water until there were no yellow droplets. In the end, we dry them in a drying oven (85°C ; 2 h) for 2 h.^{13,14}

Leaching Silk Processing of Carbon Fiber by the Dispersants.

Putting appropriate treated carbon fibers into different concentrations of dispersant emulsion for 30 min (the liquid–solid ratio of the dispersant to carbon fiber was 1:80). Cut the carbon fiber into a length of short silk after putting them in a drying oven (100°C) for two hours. Then, we cut carbon fibers into 5 mm.

Characterization of Dispersion Effects

The Method of Setting Time. Put about $0.0500 \times \text{g}$ carbon fibers that were immersed in different emulsion into 1 L solvent naphtha S60n, respectively, and then gently shake to make it achieve the optimum state. Wait for the moment when there was no obvious change for sedimentation and cluster phenomenon and record the settlement time (T).¹⁵ In each group to repeat 10 times less on average.

The Method of Turbidity Value. Respectively, put about $0.0150 \times \text{g}$ carbon fibers that were immersed in different concentration into turbidity sample bottle which included 30 mL solvent naphtha S60n and then gently shake 10 times up and down. When there was no air bubbles put it in turbidity meter to measure the turbidity value of the carbon fiber dispersion.^{8,11} In each group to repeat 10 times less on average.

The Method of Oscillation Observation. Respectively, put about $0.0500 \times \text{g}$ carbon fibers that were immersed in different concentration into stoppered cylinder which included 30 mL solvent naphtha S60n. Observe dispersion effect and take a picture by digital cameras.

The Characterization of the Carbon Fibers Surface Morphology Structure and Chemical Composition

The ATR-FT-IR Characterization of the Carbon Fibers Surface. Attenuated total reflection infrared spectrometer (ATR-FT-IR) is a surface-attenuated total reflection spectroscopy with good sensitivity and selectivity and it can be used to analyze chemical composition of the fiber surface. In this article, ATR-FT-IR was used to character the chemical composition of the carbon fiber surface before and after dipping wire. The range of the testing wave number is $4,000\text{--}500 \text{ cm}^{-1}$ and the resolution is 4 cm^{-1} .

The XPS Characterization of the Carbon Fibers Surface. X-ray photoelectron spectroscopy (XPS) is an important means which can analyze solid surface composition and study the electronic energy state of the surface. It is mainly used for qualitative and quantitative analysis of surface composition. In many cases, XPS can determine the surface composition and valence electron without loss, so it has been widely applied in surface analysis techniques. Before the measurement, sample must be cleaned in anhydrous ethanol by ultrasonic and then be dried.

The FE-SEM Characterization of the Carbon Fibers Surface.

Field emission scanning electron microscope (FE-SEM) is a surface structure analytical device with high resolution and its magnification can be regulated continuously. In this article, we

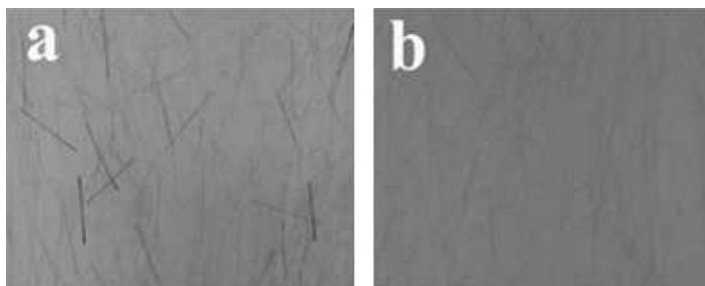


Figure 1. The dispersion diagram of carbon fiber in oil matrix; (a) CF and (b) CF-MLBH.

use it to observe the three dimensional morphology structure of carbon fiber surface before and after dipping wire. Before observing, the samples should be dried fully and then be gilded in a vacuum for 15 min.

The STM Characterization of the Carbon Fibers Surface.

Scanning tunneling microscope (STM), with atomic-level high resolution, is a detecting material surface structure instrument using the tunnel effect in quantum theory and the real-time three-dimensional images of the carbon fiber surface can be obtained by STM. In this article, we use it to observe the structure of carbon fiber before and after dipping wire, and the processed three-dimensional color image could be used to estimate the dispersion. However, before observing, the samples should be dried fully and then be handled according to the rules. Lastly, the corresponding morphology pictures should be handled by PHOTOSHOP and MATLAB.

RESULTS AND DISCUSSIONS

The Decentralized State of Carbon Fiber in Oily Matrix

In the premise of the same dispersion process, the carbon fiber decentralized states in an oily matrix that is processed with MLBH dispersion and without MLBH dispersion are shown in Figure 1. Without the treatment of dispersion MLBH, the distribution of carbon fiber in the oily matrix is uneven with fibers entangling each other and bonding bundles. So the decentralized state is poor and there has more obvious segregation phenomenon in the oily matrix. However, the dispersion of fiber in the oily matrix is even comparatively and the state of carbon fibers in the oily matrix is suspended and the compatibility is good when the carbon fiber is processed by MLBH.

The Effect of MLBH Concentrations on Sedimentation Time, Turbidity, and Dispersion Effect

The effect of MLBH concentration on dispersion effect of carbon fiber is shown in Table II and Figures 2 and 3. As shown in table and figures, the optimum leaching concentration of

Table II. The Effect of MLBH Concentration on the Dispersion of Carbon Fiber

Dispersant concentration (%)	0.0	0.1	0.2	0.3	0.4	0.5
Dispersion effect ^a	--	-	+	++	+ -	-

^a“++” means “Good”; “+” means “Better”; “+ -” means “General”; “-” means “Worse”; and “--” means “Bad”.

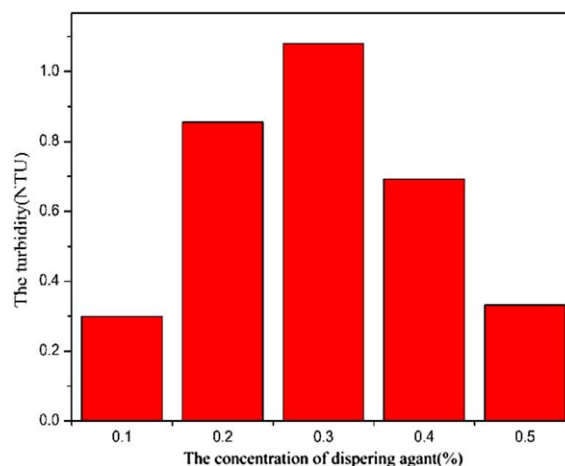


Figure 2. The impact of dispersant concentration on the turbidity values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

MLBH is 0.3%. In the preferred concentration of dipping carbon fiber has the maximum turbidity value, the longest settlement time and the best dispersion effect compared with others. The turbidity value and settlement time is 1.081 NTU and 28 min, respectively. The best carbon fiber dispersion effect, the maximum turbidity value and longest settlement time are achieved in the optimum dipping concentration because the

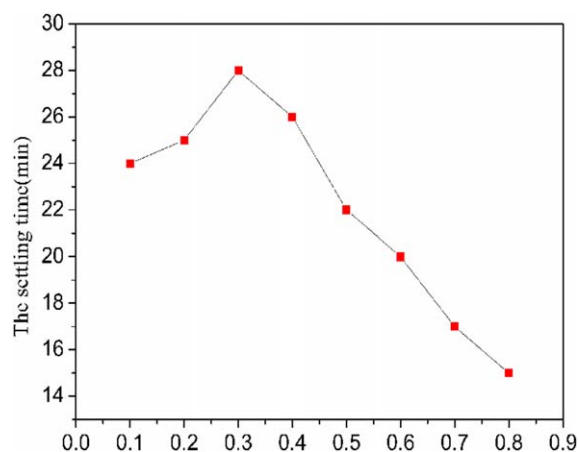


Figure 3. The impact of dispersant concentration on the settling time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

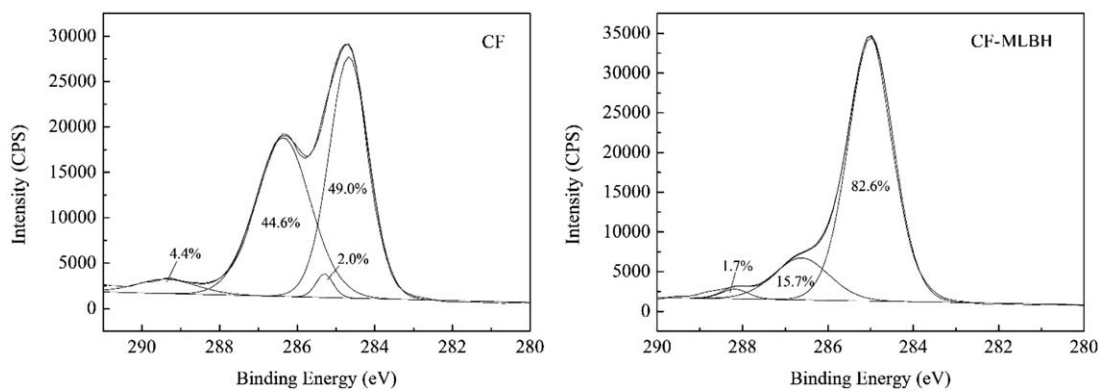


Figure 4. The peak spectra of carbon fiber before and after dipping in MLBH Solution.

dispersant could spread out on the surface of carbon fiber almost completely and the friction and absorption between adjacent carbon fibers achieved their minimum. In the lower dipping concentration the inferior dispersion effect of carbon fiber in the oil materials are obtained due to the incomplete spreading dispersant on the surface of carbon fiber and excessive friction between adjacent carbon fibers. When in the higher dipping concentration the inferior dispersion effect of carbon fiber in the oil materials is due to the too much coverage dispersants on carbon fiber surface and high viscosity between adjacent carbon fibers.^{5,12}

The Surface Chemical Composition Test and Analysis of Carbon Fiber Dispersion

Figure 4 shows the C_{1s} XPS peak spectra of carbon fiber before and after dipping in MLBH. The spectrum of C_{1s} after peak processing consists of four peaks and they are the graphite carbon that is in the form of C—C key (284.3 eV), the hydroxy (C—OH, 285.49–285.77 eV), the carbonyl (C=O, 286.28–286.98 eV), the carboxyl (COOH), or the ester (COOR, 287.97–288.56 eV), respectively. As can be seen, all kinds of oxygen-containing functional groups on the surface decreased significantly when carbon fibers were treated by dispersant. This is because dispersant MLBH evenly covered the surface of carbon

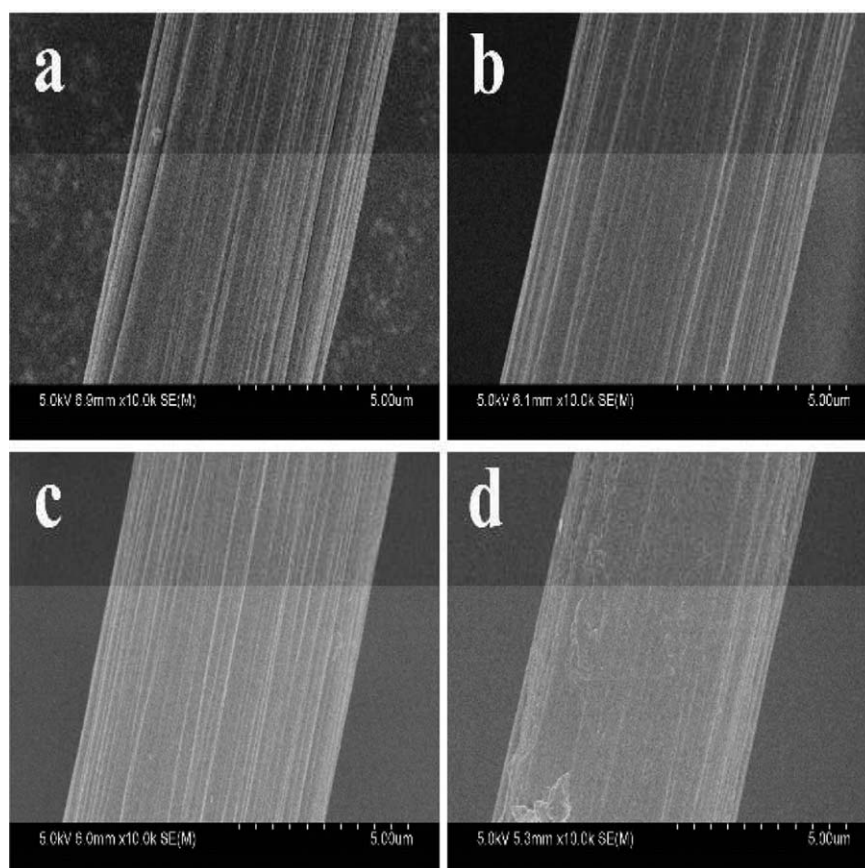
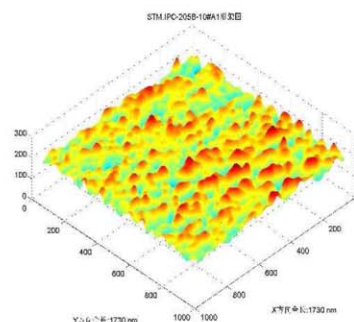


Figure 5. The FE-SEM images of carbon fiber before and after dipping in MLBH solution: (a) 0.0%; (b) 0.2%; (c) 0.3%; and (d) 0.4%.



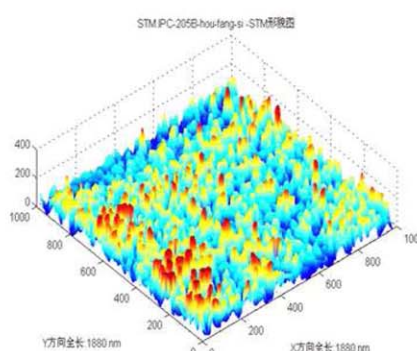
(a) The Gray-scale figure of concentration is 0.2%



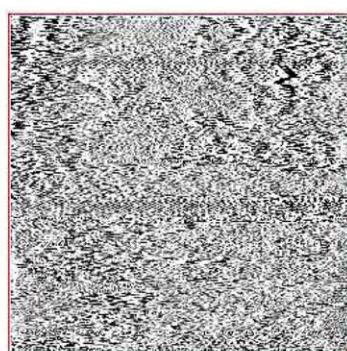
(d) The surface topography of concentration is 0.2%



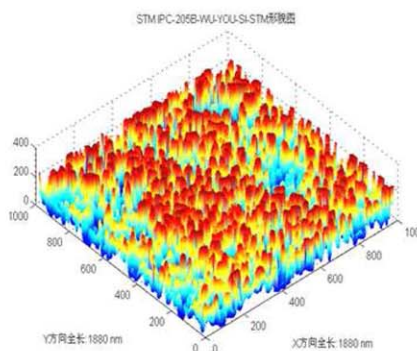
(b) The Gray-scale figure of concentration is 0.3%



(e) The surface topography of concentration is 0.3%



(c) The Gray-scale figure of concentration is 0.4%



(f) The surface topography of concentration is 0.4%

Figure 6. The STM images of carbon fiber before and after dipping in MLBH Solution. (a) The Gray-scale figure of concentration is 0.2%, (b) The Gray-scale figure of concentration is 0.3%, (c) The Gray-scale figure of concentration is 0.4%, (d) The surface topography of concentration is 0.2%, (e) The surface topography of concentration is 0.3%, and (f) The surface topography of concentration is 0.4%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fibers and thus changed the surface functional groups of carbon fiber.

The Surface Morphology and Structure Test Analysis of Carbon Fiber Dispersion

The carbon fiber dipped in different concentrations of dispersion was tested by SEM, and the test result is shown in Figure 5. As shown in Figure 6, the varying degrees of spreading formed on carbon fiber surface is due to the adsorption and the complex effect when carbon fiber was dipped in different dispersion concentrations. Dispersant could spread completely on

the surface of carbon fiber in the optimum dipping concentration; the dispersants cannot spread evenly on the surface of carbon fiber in the lower concentration with many ditches on the carbon fiber surface meanwhile; too much dispersant covered the carbon fiber surface in the higher concentration and many protuberances formed on carbon fiber surface to some extent. The varying degrees spreading on carbon fiber surface will affect the friction, adsorption, adhesion, etc., which demonstrates that the dispersion effect of carbon fiber in the optimum dipping concentration is the best compared with those in the other dipping concentrations.^{13,14}

The carbon fiber dipped in different concentrations of dispersion was tested by STM and the test result is shown in Figure 6. As shown in Figure 6(a,c,e) is Gray-scale figures after dipping in the concentration of 0.2%, 0.3%, and 0.4%, respectively. And in Figure 6(b,d,f) is surface shape appearance figures after being processed by PHOTOSHOP and MATLAB. In the figures, the points at the same height are joined together with straight lines or curves and the other intersections are found by the linearization technique.^{15,16} From the Figure 6(a,c,e), we can see that the number of brightness variance stripes decreases and then gradually increases along with the increasing dipping concentration and the scans of the carbon fiber dipped in the concentration of 0.3% is the best. As shown in Figure 6(f), in the carbon fiber topography, the surface was rough and the dispersal uniformity of dispersant on the fiber surface became worse when the dipping concentration is >0.3%. The field emission scanning electron microscope images and the scanning tunneling microscope images indicated that the dispersion effect of carbon fiber in the optimum dipping concentration is the best compared with the other concentrations.¹⁶

The Analysis of the Dispersion Mechanism

The main dispersing mechanism for the dispersion of carbon fiber in the matrix was drawn as follows: the dispersant was stuck to carbon fiber surface through strong interaction and then dispersed well or dissolved in the matrix, so that the carbon fiber could disperse in the matrix. MLBH as the oil-soluble dispersants, it can improve the dispersion of carbon fiber in oil material significantly. MLBH has favorable dispersion in the matrix of oil material, and when the dispersant formed on the surface of the carbon fiber, it can filled the ditches and formed well-distributed coating on surface of the carbon fiber and decreased the friction and absorption between adjacent carbon fiber, then the carbon fiber could disperse rapidly. However, MLBH is also a kind of anion dispersant, after the carbon fiber dipped in dispersion it can improve the lubricity and repulsive force between adjacent carbon fibers by adding more like charges on carbon fiber surface, and the good dispersion effect of the carbon fiber could be obtained.

CONCLUSIONS

It is very effective to improve the dispersion state of carbon fiber in the oily materials by MLBH dispersant. Dispersants

would spread completely on the surface of carbon fiber and the turbidity gets its maximum value and the settlement time is the longest when the leaching silk concentration of MLBH is 0.3%.

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