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Carbon nanotubes loaded with Fe_3O_4 particles to enhance electromagnetic shielding of PAM/L hydrogels

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1. Experimental

1.1 Materials

Acrylamide (AM, AR), Ammonium Persulfate (APS, AR), N, N'-Methylenebisacrylamide (MBI, AR), NaOH (AR), urea (AR), sodium nitrate (AR), Ferric chloride hexahydrate (AR) purchased from Aladdin Reagent (Shanghai) Co. Ltd. and carbon nanotubes (CNTs) purchased from Suzhou Tanfeng Graphene Technology Co., Ltd. Linum fiber (length 106.5 mm) was purchased from Dongguan Kaiye Textile Industry Co. The purified water utilized in the study was prepared using a water purifier.

1.2 Preparation of Linum fiber solution

The alkaline/urea aqueous solution system was selected for this experiment, and the sodium hydroxide/urea aqueous solvent was prepared by combining sodium hydroxide, urea, and deionised water in the ratio of 8:12:80 by mass. The solvent was pre-cooled to -12 °C. Then, a certain amount of Linum fiber was weighed and magnetically stirred for 30 min to obtain a 2% flax cellulose solution.

1.3 Preparation of PAM/L/CNTs hydrogels

Firstly, 2 g of Linum fiber solution was weighed and slowly poured into a beaker, followed by the addition of 2 g of acrylamide (AM), a certain amount of initiator ammonium persulfate (APS) and cross-linking agent N'N-methylenebisacrylamide (MBA), followed by magnetic stirring for 40 min, and then the addition of carbon nanotubes (CNTs) to the mixed solution and stirring for 10 min, after which the solution was The mixture was poured into a silicone mold and left at room temperature for 30 min to cross-link to form a PAM/L/CNTs hydrogel. The series of composite hydrogels prepared were named as PAM/L, PAM/L/1-CNTs, PAM/L/2-CNTs, PAM/L/4-CNTs, and PAM/L/6-CNTs according to the different carbon nanotube additions.

1.4 Preparation of Fe_3O_4@CNTs by hydrothermal synthesis method

Firstly, 0.1 g of CNTs, 1 g of ferric chloride hexahydrate and 60 ml of deionized water were weighed and mixed homogeneously, and then 2 g of $NaNO_3$ was added and ultrasonicated for 30 min, and then transferred to a hydrothermal reactor, and after standing for 2 h, it was transferred to a blast drying oven at 60 ℃ and kept for 12 h. At the end of the reaction, the reaction product was taken out, and washed repeatedly with deionized water. Finally, the washed products were transferred to a blast drying oven at 60 ℃ for 12 h to obtain Fe_3O_4@CNTs composites.

1.5 Preparation of PAM/L/Fe_3O_4@CNTs hydrogels

Weighing 2 g of flax cellulose solution was slowly poured into a beaker and stirred, followed by the addition of 2 g of acrylamide (AM), a certain amount of initiator ammonium persulfate (APS) and cross-linking agent, followed by magnetic stirring for 40 min, and then Fe_3O_4@CNTs was stirred before adding Fe_3O_4@CNTs to the mixed solution, which was then poured into silica gel moulds and allowed to stand for 30 min in a room-temperature environment to allow for the formation of a cross-linking PAM/L/Fe_3O_4@CNTs composite hydrogel. Depending on the amount of Fe_3O_4@CNTs added, a series of composite hydrogels, referred to as PAM/L/1-Fe_3O_4@CNTs, PAM/L/2-Fe_3O_4@CNTs, PAM/L/4-Fe_3O_4@CNTs, PAM/L/6-Fe_3O_4@CNTs.

1.6 Characterization

SEM (Quanta FEG 250, FEI Company) was used to observe the morphology of the hydrogels, The test voltage is 20.0 kV. The hydrogel samples were freeze-dried and ground into powder, and the samples were scanned under an infrared spectrometer probe with a resolution of 8 cm^{-1} and a test range of 500-4000 cm^{-1} with 32 scans. For XRD analysis of hydrogels, the voltage applied during the test was 40 kV, the current was 40 mA, the scanning angle was 10-90°, and the scanning rate was 2 °/min. The thermal properties of hydrogels were analysed using DSC. The melting curves were obtained by taking 5-10 mg of the samples in a crucible and cooling them from 40 ℃ to -40 ℃ with a cooling rate of 10 ℃/min and then warming them from -40 ℃ to 40 ℃ with a warming rate of 10 ℃/min under the protection of N_2. The water content of the samples was measured as the mass of the hydrogel before and after 24h. The compression properties of hydrogel were tested using a microcomputer-controlled electronic universal testing machine at room temperature, with the transducer set to 1000 N, the preload force set to 0.005 N and the compression rate set to 100 mm/min. A four-probe tester was used to test the conductivity of hydrogel samples, where the hydrogel samples were rectangular in shape and the dimensions of the test samples were 20 mm × 10 mm × 3 mm. The electromagnetic shielding performance was tested by a vector network analyzer, after calibrating the instrument and setting the frequency range to X-band (8.2-12.4 GHz). In this way, the scattering parameters of the samples (i.e., S11 and S21) are obtained, and then the total electromagnetic shielding effectiveness (EMI SET), the reflective shielding effectiveness (SER), and the absorptive shielding effectiveness (SEA) are calculated by equations (1-6):

$$R = |S_{11}|^2 \tag{1}$$

$$T = |S_{21}|^2 \tag{2}$$

$$A = 1 - (T + R) \tag{3}$$

$$SET = 10log\frac{1}{T} \tag{4}$$

$$SER = 10log\frac{1}{(1-R)} \tag{5}$$

$$SEA = 10log\frac{(1-R)}{T} \tag{6}$$