

Characterizations of the surface charges by zeta potential test and by point zero charge (PZC) test

(Supplementary Material)

1. Materials and Methods

1.1 Solid surface Zeta potential test

SFAL, SFAL-SF, SFAL-SA, SFAL-SF/SA, SFAL-SF-CaP, SFAL-SA-CaP and SFAL-SF/SA-CaP groups were prepared. The surface charges of these samples were tested by Solid Surface Zeta Potential Analyzer (SurPASS 3, Anton Paar, Austria) at Institute of Urban Environment, Chinese Academy of Sciences. The test was carried out at pH 6, 7, and 8.

1.2 Point of zero charge (pH_{ZPC})

The PZC tests of SFAL, SFAL-SF:SA=5:5 and SFAL-SF:SA=5:5-CaP groups were carried out by solid addition method¹⁻³. The method is described as follows. 0.01 M NaCl, 0.1 M HCl and 0.1 M NaOH solutions were prepared. The initial pH values of 0.01 M NaCl were controlled at 4.0, 5.0, 6.0, 7.0 and 8.0 by adding 0.1 M HCl or NaOH, and then, the NaCl solutions with different pH values were preserved in sealed centrifuge tube. 0.1 g of each sample and 10 mL NaCl solutions with different pH were placed in different brown bottles, respectively. The solutions were sealed for 24 h, and the final pH values of the solutions were determined. If the pH is not changed, the PZC is the final pH.

2. Results and Discussion

2.1 Solid surface Zeta potential test

The results of solid surface Zeta potential test are shown in table 1. All samples show negative charges and no distinct differences can be found except for SFAL at pH 8, SFAL-1%SF at pH 7 and pH 8. These results are in line with previous ones showing that silk fibroin is prone to be negatively charged under alkaline conditions. In addition, regenerated silk fibroin is more sensitive than natural fibers. However, no obvious changes were seen in other samples.

Table 1 The solid surface zeta potentials of the samples

Zeta potential (V)	pH=6	pH=7	pH=8
SFAL	-0.02933	-0.0311	-0.3098
SFAL-1%SF	-0.03022	-0.2825	-0.2677
SFAL-1%SA	-0.02457	-0.0281	-0.03156
SFAL-SF:SA=4:6	-0.02440	-0.02035	-0.01844
SFAL-SF:SA=5:5	-0.01910	-0.02413	-0.02528
SFAL-1%SF-CaP	-0.02708	-0.02779	-0.02065
SFAL-1%SA-CaP	-0.02313	-0.02619	-0.02999

SFAL-SF:SA=4:6-CaP	-0.02547	-0.02682	-0.02311
SFAL-SF:SA=5:5-CaP	-0.02373	-0.02848	-0.02998

2.2 Point of zero charge (pH_{ZPC})

The results of pH_{PZC} are shown below (table 2) and show that the pH_{PZCS} of SFAL, SFAL-SF/SA, and SFAL-SF/SA-CaP are likely 8.0, 7.0, and 7.0, respectively. The results are in agreement with the above ones obtained by Solid Surface Zeta Potential Analyzer. This method is indeed facile, powerful and helpful.

Table 2 The PZC tests results of the samples

The final pH	pH=4.0	pH=5.0	pH=6.0	pH=7.0	pH=8.0
SFAL	7.2	7.5	8.0	7.4	8.0
SFAL-SF/SA	6.7	7.2	7.2	7.2	7.6
SFAL-SF/SA-CaP	6.7	6.9	6.9	6.9	7.0

The surface properties are important for the comprehension of interfacial interactions of the surfaces with ions. To explain the complicated mechanisms, more work is needed to draw a confirmative conclusion. In the future work, both methods will be employed to explore the charge performance (PZC) of more biomaterials extensively, systematically and in depth. A more comprehensive study will be carried out.

References

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