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Quaternization on polyetheretherketone and its antimicrobial activity

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ABSTRACT

Polyetheretherketone (PEEK) is a thermoplastic polymer with high performances, especially behaving an elastic modulus closer to that of human bone, and has been a good candidate for implants in orthopedics and trauma. But infections arising from the use of implants or the surgical site contaminant are very common in surgery. So in this study, PEEK was firstly chloromethylated to get CM-PEEK, which was separately grafted with two kinds of quaternary ammonium salts and successfully made two different antibacterial surfaces (S-PEEK and C-PEEK). The results indicate that the wettability of both surfaces was largely improved, and both S-PEEK and C-PEEK exhibited an antibacterial rate of over 98% to S. aureus and over 48% to E. coli. This study suggests that quaternization on PEEK might be an excellent method to make antibacterial biomaterials with high wettability.

1. Introduction

Polyetheretherketone (PEEK) is a linear homopolymer composed of single repeating units interconnected by one ketone bond and two ether bonds [1,2]. PEEK possesses outstanding performances in mechanical strength, thermal & chemical stability, and non-toxicity, especially its elastic modulus closer to that of human bone in comparison with other polymers. PEEK biomaterials have already played a key role as a candidate to be used in prosthetics, and highly performed as implants particularly for spine fusion and joint replacement. But it is well known that infections arising from the use of implants or the surgical site contaminant are very common in surgery, no matter in the early phase after implantation or even after the completion of tissue integration [3]. And silver [4], graphene [5], quaternary ammonium salt [6], antimicrobial peptides [7] and so on have ever been used to make up the antimicrobial deficiency of most substrates, among which quaternary ammonium salt, formed by a hydrocarbon group replacing four hydrogen atoms in an ammonium ion, is a new kind of antimicrobials appeared in 1990s. And its antibacterial effect is fulfilled by absorbing and contacting bacteria [6], which is effective to reduce or avoid the resistance of bacteria against antibacterials. So in this study, quaternary ammonium salts were selected to modify and functionalize PEEK biomaterial.

2. Materials and methods

2.1. Materials

PEEK was purchased from Jilin Joinature Polymer Co., Ltd., China. Chloromethyl octyl ether (CMOE), N-Methyl pyrrolidone (NMP), octadearyl dimethyl ammonium chloride (STAC) and hexadecyl trimethyl ammonium bromide (CTMAB) were supplied by Shanghai Aladdin Co. Ltd., China.

2.2. Preparation of chloromethylated PEEK (CM-PEEK) and quaternized PEEK

1 g PEEK powders were dissolved in 60 ml 92.8 wt% concentrated sulfuric acid at 0 °C with stirring for 90 min. Then lowered the temperature to −10 °C, followed by the addition of 8 ml CMOE with stirring for 90 min to get CM-PEEK, which was separated from the mixture by precipitation in ice water and finally vacuum-dried under 80 °C.

1 g CM-PEEK, 1.86 g STAC and 1.95 g CTMAB were respectively dissolved into NMP to get 3 homogeneous solutions. Then added STAC and CTMAB solution to CM-PEEK solution separately and reacted for 12 h at 80 °C to get the final quaternized PEEK (S-PEEK and C-PEEK).

2.3. Measurements

^{1}H NMR spectroscope (Bruker AV II, 400 MHz) was used to confirm the successful synthesis of CM-PEEK. CM-PEEK solution was prepared by dissolving it into DMSO d_6 solvent.

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CM-PEEK, S-PEEK and C-PEEK were measured by fourier transform infrared spectroscopy (FTIR, Nicolet 6700, US) for analyzing the compositions. The wettability of S-PEEK and C-PEEK was characterized by measuring the contact angle of specimens using JY-82A video contact angle measuring instrument. The surface elemental composition was analyzed by X-ray photoelectron spectroscope (XPS, XSAM800 UK). The surface morphologies of all samples were observed using a scanning electron microscope (SEM, Inspect F50, Netherlands).

Escherichia coli (E. coli, gram-negative) and Staphylococcus aureus (S. aureus, gram-positive) were commonly used as model bacteria to evaluate the antibacterial activity of materials. Here, two methods were adopted to determine the antibacterial effect, one is qualitative detection (growth inhibition zone for bacteria), the other one is quantitative measurement (plate-counting method). For the former, the materials were made into disk and placed on agar plates coated with bacteria, incubated for 24 h in an incubator at 37 °C. For the latter, the materials were contacted with the bacterial fluid for 2 h. Ten-fold dilution method was used to count the number of bacterial colonies until up to 30–300 CFU (colony-forming unit) [8] after coating the bacterial liquid on solid agar medium, and thus deduced the initial bacterial concentration. Bacteriostasis rate (BR), reflecting the antibacterial ability, was defined by the Eq. (1) [8].

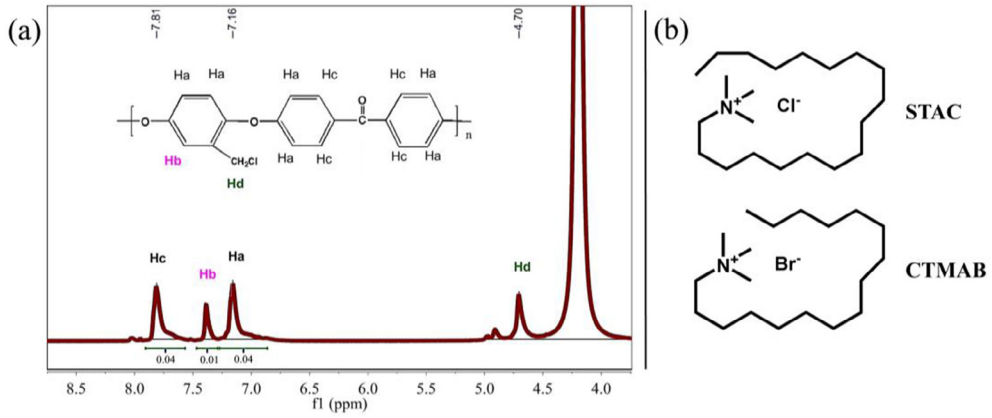

Fig. 1. (a) ^{1}H NMR spectra of CM-PEEK, and (b) the structural formulae of STAC and CTMAB.

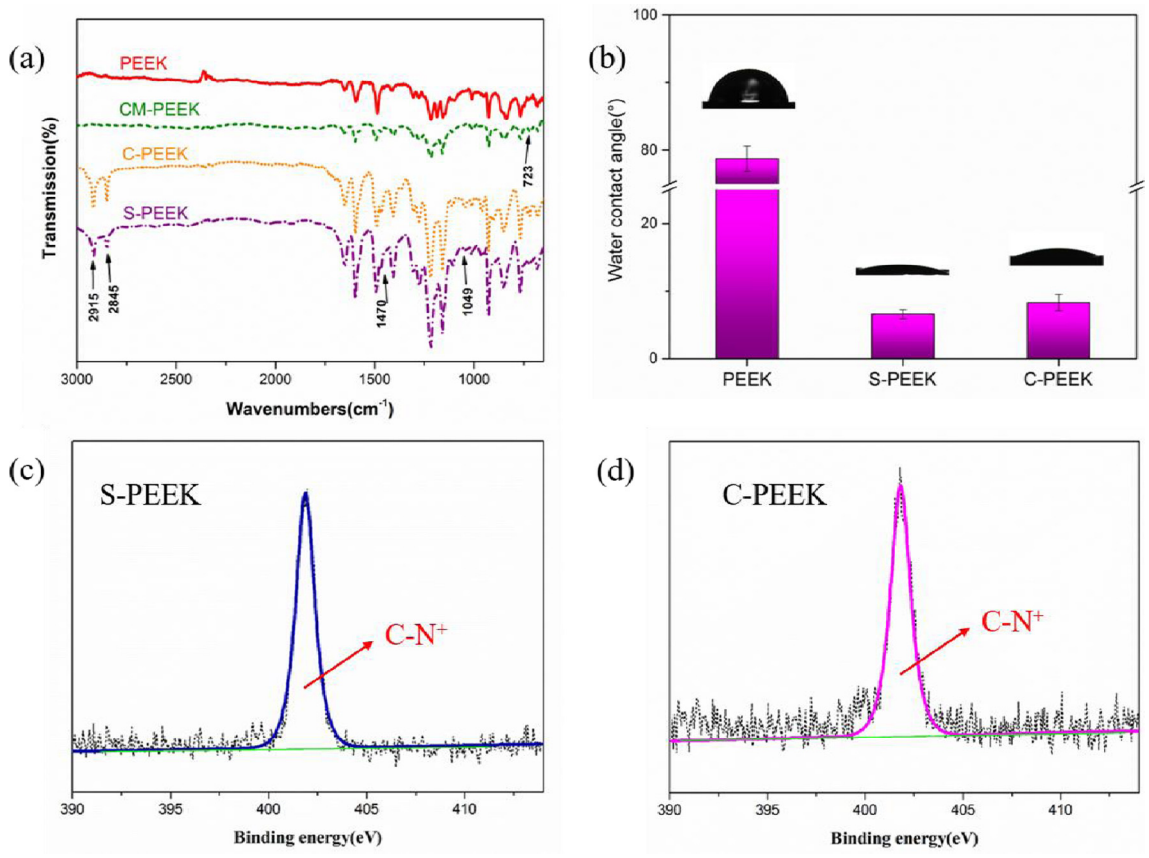

Fig. 2. (a) IR spectra, (b) images of the water contact angle, XPS spectra of S-PEEK (c) and C-PEEK (d).