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Synthesis and properties of PDMS/montmorillonite-cetyltrimethylammonium bromide-heparin films

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ABSTRACT

In this study, poly(dimethylsiloxane)(PDMS)/montmorillonite-cetyltrimethylammonium bromide-heparin (PDMS/MMT-CTAB-HEP) films were prepared by solution intercalation technique. The cetyltrimethylammonium bromide-heparin (CTAB-HEP) was intercalated into montmorillonite (MMT) layers forming MMT-CTAB-HEP (modified MMT). The structure and properties of the film were characterized by XRD, TG and SEM.

The modified MMT was homogeneously dispersed within the PDMS matrix. The effect of modified MMT on mechanical properties of the film was also investigated. As the modified MMT content was lower than 2 wt%, the films showed excellent mechanical properties. The blood compatibility of PDMS/MMT-CTAB-HEP films was further evaluated by hemolysis test and platelet adhesion. Both hemolysis and platelet adhesions tests showed that PDMS/MMT-CTAB-HEP film had better blood compatibility than pure PDMS.

1. Introduction

Polymeric materials are widely used in biomedical applications (Mani, Feldman, Patel, & Agrawal, 2007; Mark, Anthony, Mark, & Van, 2007), especially in medical device development. However, blood compatibility is still one of the major problems facing the biomedical applications of these polymers (Lee & Messersmith, 2007; Tanzi, 2005; Woolfson & Ryadnov, 2006).

Poly(dimethylsiloxane) (PDMS) based materials have been applied to various medical devices due to its attractive properties of high oxygen permeability, optical transparency, self-sealing property, convenient processability and chemical stability (Kaneko & Yoshida, 2008; Yuan et al., 2010). However, thrombosis still occurs when they are used as blood contact materials, so more and more attentions have been paid to improve the blood compatibility of PDMS (Rao, Zhang, & Liu, 2013).

Polymer layered silicate (PLS) nanocomposites often have enhanced thermal, mechanical, and barrier properties as compared to the pure polymer, even with very low silicate mass contents (Pavlidou & Papaspyrides, 2008). In recent years, polymer nanocomposites with various clays have been extensively investigated due to their cost effectiveness and potential applications in different fields, including the structural, electronics, aerospace, and biomedical industries (Akat, Tasdelen, DuPrez, & Yagci, 2008; Islam, Khana, & Park, 2012; Liu, Chaudhary, Yusa, & Tade, 2010).

Montmorillonite (MMT) clay is one of the smectite group, composed of silica tetrahedral sheets layered between an alumina octahedral sheets. MMT has large specific surface area; exhibits good adsorption ability, cation exchange capacity, standout adhesive ability, and drug-carrying capability. Thus, MMT is a common ingredient as both the excipient and active substance in pharmaceutical products (Wang, Du, & Luo, 2008).

Heparin is a negatively charged natural-occurring linear polysaccharide chain composed mainly of repeating units of sulfonated glucuronic acid and glucosamine derivatives (Christensen, Larsson, Emanuelsson, Elgue, & Larsson, 2001; Munoz & Linhardt, 2004; Wu, Grinnell, & Meyerhoff, 2007). It is an important anticoagulant that clinically used to minimize thrombus formation on artificial surfaces. It has the ability to interact

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strongly with antithrombin III to prevent the formation of fibrin clot.

In this study, we prepared novel PDMS/cetyltrimethylammonium bromide-heparin (CTAB-HEP) modified montmorillonite films to endow anticoagulation activity. First, heparin complexed with CTAB and the resulting complex, CTAB-HEP was then intercalated into MMT layers to form a composite. Next, PDMS/modified montmorillonite films were prepared by a solution intercalation, where PDMS and modified montmorillonite were homogeneously dispersed. The structure, morphology, and physical properties of the PDMS/modified montmorillonite film were characterized by X-ray diffraction (XRD), SEM and TGA. Finally, the antithrombogenic property of the film was evaluated by hemolysis and platelet adhesion tests.

2. Experiment part

2.1. Materials

MMT (Na^+-MMT) with a cation exchange capacity (CEC) of 0.90 meq/g was supplied by Zhe Jiang Clay Minerals Co. Cetyltrimethylammonium bromide as surfactant (Sigma, USA) and heparin (sodium salt Sigma, 150 U/mg, St. Louis, MO, USA) were used as received. Hydroxyl-terminated PDMS with a number-average molecular mass of 50,000 (Beijing, China) was used as received. All other chemicals were of analytical grade and used as received. Fresh whole blood was collected from consenting donors by Jiangsu blood center with ethics approval.

2.2. Preparation of the MMT-CTAB-HEP(OMMT)

In 50 ml distilled water, 1 g of Na-MMT was suspended and stirred for 1 h at room temperature. The mixture of 1 g of CTAB and 1 g of heparin was slowly added into MMT dispersion. The mixture was then stirred for 2 h at 80 °C and ultracentrifuged at 12 000 rpm for 1 h. The precipitate was filtered, washed with distilled water. The resultant product was dried in vacuum at 60 °C until constant weight.

2.3. Preparation of modified MMT-PDMS composite films (PDMS/MMT-CTAB-HEP composite films)

The volume fraction of the modified MMT was varied from 0 to 3 wt%. The desired amount of the modified MMT was added to a solution of PDMS in cyclohexane. The mixture was sonicated for 5 min. Then tetraethyl orthosilicate (TEOS, as crosslinking agent), was added, followed by addition dibutyltin diacetate (Sn) (Aldrich). The dispersion was mixed by agitation and stirring at room temperature under vacuum to remove gases generated during crosslinking. After one week, the cured samples were taken for analysis.

2.4. Characterization

The X-ray diffractometer (D/max-rC, Rigaku) was operated in the speed of 2°/min and the angular range was 0.5–40° (2θ) for X-ray powder diffractometry (XRD) analysis. The thermogravimetric measurements were performed on a Perkin-Elmer TG 7 instrument using a heating rate of 20 °C/min up to 800 °C in nitrogen atmosphere. Scanning electron microscopy (SEM, JEOL JSM-5610LV) was used to examine the surfaces of the film samples. The film samples were coated with gold, according to standard procedures, prior to the scan analysis. The mechanical properties of the films were evaluated by measuring the tensile strength and elongation at break with using an Instron 4466 all-purpose tester at a speed of 200 mm/min.

2.5. Blood compatibility

2.5.1. Quantification of platelet adhesion

The platelet adhesion test was performed in static conditions as previously described (Lee, Ju, & Kim, 2000; Rodrigues, Gonçalves, Martins, Barbosa, & Ratner, 2006). The surface of the film samples were washed three times with double-distilled water and placed into the wells of 24-well culture plates in contact with 2 ml of human PRP and were incubated in 5% CO_2 at 37 °C for 120 min. Afterwards, the supernatants were discarded, and the samples were rinsed twice with phosphate-buffered saline (PBS) to remove the proteins and non-adherent platelets. The platelets adhering on the specimens were fixed with 2.5% gluteraldehyde for 30 min. After the fixation, the samples were washed and dehydrated in a graded ethanol series of 50%, 70%, 80%, 95% and 100% (twice) for 10 min each. The samples were freeze-dried, then sputter-coated with gold for SEM observation.

2.5.2. Hemolysis test

This assay was carried out on PDMS/MMT-CTAB-HEP films. The PDMS/MMT-CTAB-HEP films were cut into 5.5-mm-diameter pieces. Fresh anticoagulated blood from human volunteers (2 ml) was diluted with 2.5 ml of normal saline solution. The PDMS/MMT-CTAB-HEP films were prepared in normal saline solution and kept at 37 °C for 30 min. The diluted blood (0.2 ml) was added to PDMS/MMT-CTAB-HEP films. The mixture was kept at 37 °C for 60 min and then centrifuged at 1500 rpm for 10 min. The supernatant was transferred to a 96-well plate where the absorbance was measured at 545 nm using a BioTek synergy 2 Multi-Mode Microplate Reader. The mean value of three measurements was calculated. Positive controls consisted of 0.2 ml diluted blood in 10 ml deionized water while negative controls consisted of 0.2 ml diluted blood in 10 ml normal saline solution. Hemolysis degree was calculated as:

$$\%\text{Hemolysis} = \frac{\text{Absorbance of test polymer} - \text{Absorbance of negative control}}{\text{Absorbance of positive control}} \times 100$$

3. Results and discussion

3.1. X-ray diffraction (XRD)

The XRD patterns of MMT and MMT-CTAB-HEP were given in Fig. 1. MMT exhibited a broad 0 0 1 reflection with $d = 1.53$ nm (Gao, Gu, Song, Li, & Liu, 2008). The MMT-CTAB-HEP showed a very strong (0 0 1) reflection at $d = 4.01$ nm (Fig. 1). Compared to that of MMT, the interlayer spacing of the MMT-CTAB-HEP had expanded, indicating that the CTAB-HEP complex intercalated into the MMT. The interlayer spacing (Ic) of CTAB intercalated MMT was about 1.86 (Xiong, Liu, Yang, & Wang, 2004). This increase of gallery distance is possibly due to the longer alkyl chain length resulting from attachment of heparin on CTAB.

An important measure of the degree of silicate dispersion and exfoliation is usually obtained by XRD measurements. Generally intense reflections in the range $2\theta = 3 - 9°$ indicate an ordered intercalated system with alternating polymer/silicate layers. XRD patterns with no distinct features in the low 2θ range are anticipated due to the loss of structural registry (Ma, Xu, Ren, Yu, & Mai, 2003). At low angle region of 2–10°, all peaks of MMT-CTAB-HEP disappeared after intercalated into PDMS (Fig. 2). This disappearance of XRD peaks suggested that highly ordered MMT

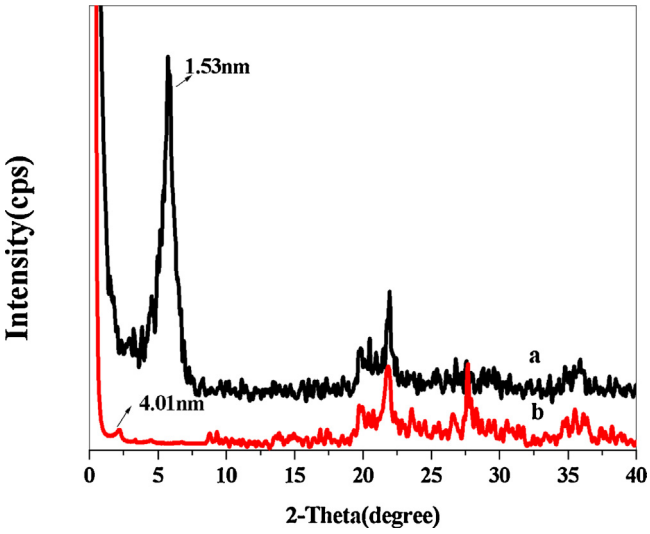

Fig. 1. XRD patterns for MMT (a) and MMT-CTAB-HEP (b).

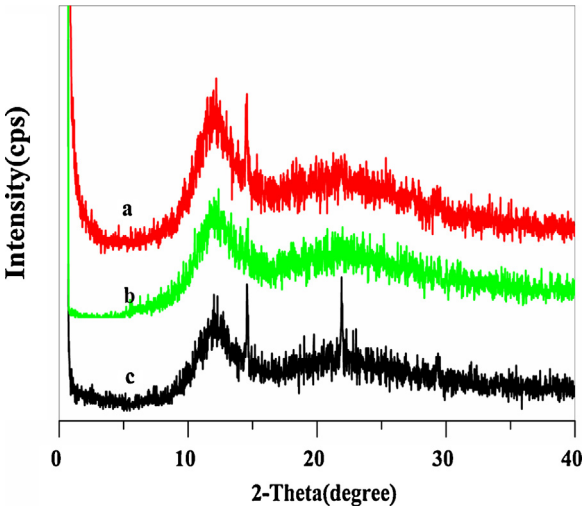

Fig. 2. XRD patterns for the composite films with 1 wt% (c), 2 wt% (d), and 3 wt% (e) MMT-CTAB-HEP.

layer structure had been completely destroyed and MMT-CTAB-HEP had been exfoliated and well dispersed into PDMS matrix.

3.2. Scanning electron microscopy analysis (SEM)

The homogeneity of the particles dispersion was investigated also by SEM (Fig. 3). The bright spots on the image represent size and particle distribution of clay aggregates. For the PDMS/2 wt% MMT-CTAB-HEP film, the finer particles appeared, although a presence of large pieces was also visible (Fig. 3a). It could be concluded that MMT-CTAB-HEP and silicone were compatible very well from the SEM spectrum, which also revealed that each lamella of MMT had been dispersed well polymer matrix. For the PDMS/3 wt% MMT-CTAB-HEP film, the dispersion of MMT-CTAB-HEP in PDMS matrix was not uniform (Fig. 3b). The particle diameter of PDMS/3 wt% MMT-CTAB-HEP film became larger, suggesting that aggregation of the particles occurred in the film (Alam, Agag, Kawauchi, & Takeichi, 2007).

3.3. Mechanical properties

Effects of organo-MMT content on the tensile strength and elongation at break of films were described in Fig. 4. Both the tensile strength and elongation at break of films increased with MMT-CTAB-HEP addition. When the MMT-CTAB-HEP content was 2 wt%, the tensile strength and elongation at break increased by about 59% and 232%, respectively. From this point on, any further increase of MMT-CTAB-HEP content causes a decrease in elongation at break and tensile strength. With increasing MMT-CTAB-HEP content, some silicate layers began to aggregate. The formation of large silicate aggregates effectively reduces the interfacial area between polymer and silicate layers. Furthermore, these aggregates act as stress concentrators to reduce the mechanical properties of films (Alam et al., 2007; Shi & Gan, 2008). Therefore, a hybrid film containing 2 wt% of the MMT-CTAB-HEP was selected as representative.

3.4. Thermal property

Thermal stability of PDMS/2 wt% MMT-CTAB-HEP film and pure PDMS was investigated by thermogravimetry (Fig. 5). The thermal stability of PDMS/2 wt% MMT-CTAB-HEP film was better than that of pure PDMS. The onset of the thermal decomposition of PDMS/2 wt% MMT-CTAB-HEP film greatly shifted toward higher temperature compared with pure PDMS. For PDMS/2 wt% MMT-CTAB-HEP film, the initial temperature of thermal degradation increased by 36 °C, compared with pure PDMS. The reasons for the improvement in decomposition temperatures of filled PDMS were probably: (1) the decomposition of the active centers of the siloxane main chains possibly became inactive when they came into contact with the filler, and (2) the interactions between the filler and PDMS increased the physical and chemical crosslinking points which prevented degradation of the siloxane chains (Alexandre & Dubois, 2000).

3.5. Platelet adhesion experiment

Platelet adhesion on the surface of a biomaterial is the most essential character in determining the hemocompatibility of a

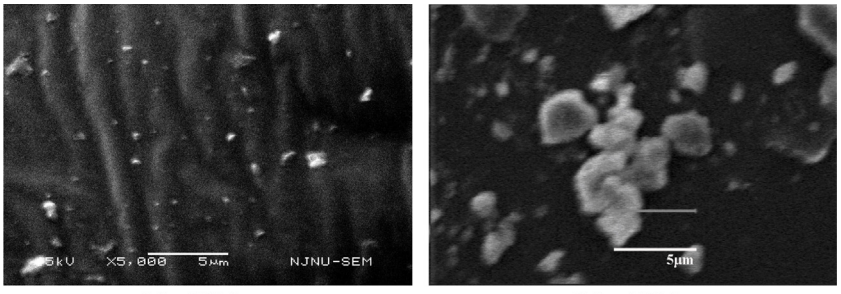

Fig. 3. SEM spectra of fracture surface from PDMS/2 wt% MMT-CTAB-HEP film (a) and PDMS/3 wt% MMT-CTAB-HEP film (b) ((a) mag. at 5000× and (b) mag. at 5000×).

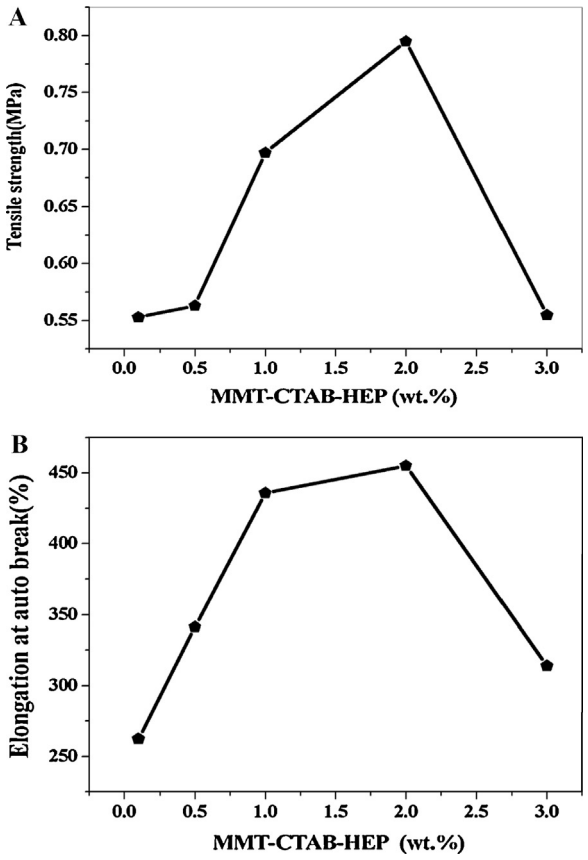

Fig. 4. The influence of the content of modified MMT on the tensile strength (a) and elongation at break (b).

biomaterial. Lower level platelet adhesion and activation denotes good hemocompatibility, while a higher degree of platelet adhesion and activation should result in the formation of a thrombus (Harker, 1994; Heijnen, Schiel, Fijnheer, Geuze, & Sixma, 1999).

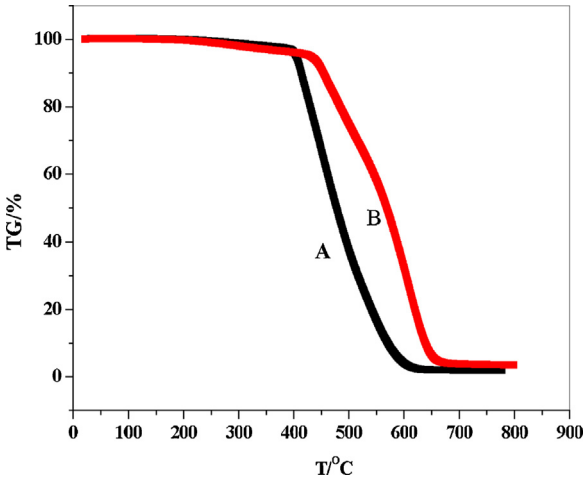

Fig. 5. TGA curves of PDMS (A) and PDMS/2 wt% MMT-CTAB-HEP films (B).

Thus, the platelet adhesion test was important to investigate the blood compatibility for biomedical materials. The film with 2 wt% MMT-CTAB-HEP showed significantly less platelet adhesion and aggregation than the pure PDMS film (Fig. 6). The platelets adhered on the surface of the PDMS/2 wt% MMT-CTAB-HEP films were not activated and the extension of pseudopodia was not observed, which was in good agreement with results of Wang and his co-workers (Wang, Lin, Liu, Sheng, & Wang, 2005). Wang and his co-workers reported that the platelet adhesion was significantly suppressed by loading heparin into zein microspheres.

3.6. Hemolysis ratio

Hemolysis of the blood is a problem associated with hemocompatibility. Red blood cells hemolyze when they come in contact with water. This problem may be aggravated in the presence of an implant material. Results obtained for hemolysis of blood with PDMS/2 wt% MMT-CTAB-HEP films were shown in Table 1. The

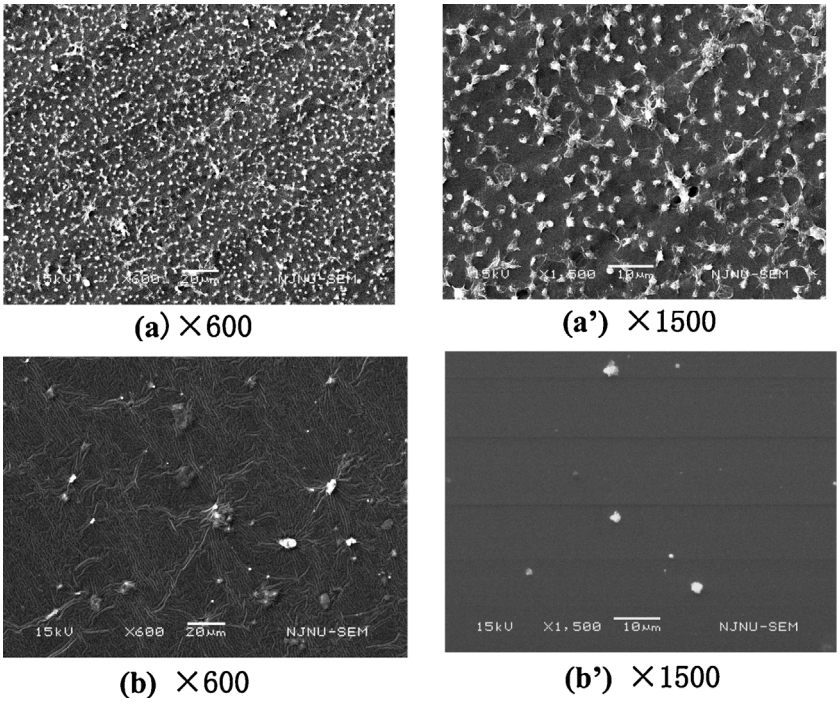

Fig. 6. SEM images of human platelet-rich plasma (PRP) incubated in PDMS (a, a′), the PDMS/2 wt% MMT-CTAB-HEP films (b, b′).

Table 1
Hemolysis of red blood cells following incubation of whole blood with PDMS/2 wt% MMT-CTAB-HEP films and PDMS.

Sample	Hemolysis (%)
PDMS	4.19
PDMS/2 wt% MMT-CTAB-HEP films	0.98
Saline	0
Distilled H_2O	100

PDMS/2 wt% MMT-CTAB-HEP films and PDMS were incubated with human blood. As a control, a blood sample was incubated in an isotonic solution under the same conditions. The ratio of released hemoglobulin from the red blood cells was accepted as 100% for blood incubated in distilled water. As shown in Table 1, the incorporation of HEP into the PDMS film resulted in a decrease in the hemolytic activity.

Hemolysis occurs when cells swell to the critical bulk to break up the cell membranes. Meanwhile, released ADP from the broken red blood cells intensifies the assembly of blood platelets, which accelerates the formation of clotting and thrombus. Heparin is a sulfated glycosaminoglycan and a highly negative charged polyanion. It is known as an effective binding agent for plasma lipoproteins. Heparin was used to remove lipoproteins from plasma in patients with severe hypercholesterolemia. In vitro studies revealed that heparin-induced extracorporeal lipoprotein precipitation also removes endotoxin, the tumor necrosis factor, and c-reactive protein (Petrini, Tanzi, Visai, Casolini, & Speziale, 2000). A significant decrease in the hemolysis rate (Table 1, 0.98) was observed, which falls well within the permissible limit (Autian, 1975). These results all indicate that PDMS/MMT-CTAB-HEP film have good anticoagulation characteristics.

4. Conclusions

The PDMS/MMT-CTAB-HEP films were prepared by a solution intercalation method. The film was characterized by XRD, SEM and TG. The PDMS/modified MMT film with 2 wt% MMT-CTAB-HEP showed the best mechanical properties in our experiment conditions. The hemocompatibility of PDMS/2 wt% MMT-CTAB-HEP films was evaluated platelet adhesion and hemolysis testing. The PDMS/2 wt% MMT-CTAB-HEP films improved resistance to platelet adhesion and decreased the hemolysis rate. This film also enhanced blood compatibility. The biopolymer materials introduced in this study are hemocompatible materials warranting further investigation for the use in blood-contacting devices.

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