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Research Article

Preparation and Characterization of Polyurethane/Nanocopper Composites and Their Application in Intrauterine Devices

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A novel intrauterine devices material, polyurethane/nano-copper (PU/NC) nanocomposite, was prepared. The structure, morphology, copper ion (Cu^{2+}) release rate, and water absorption of PU/NC nanocomposites were investigated. The results indicated that the nanocoppers were uniformly dispersed in the matrix. The release rates of Cu^{2+} of PU/NC nanocomposites remained stable during the experimentation time. These results indicated that the PU/NC nanocomposites have a great potential to replace current commercial intrauterine devices materials.

1. Introduction

The intrauterine devices (IUDs) are the most widely used reversible method of contraception in the world today [1, 2]. Use of IUD which can release Cu^{2+} *in vivo* is one of the effective and easy contraceptive methods. Postpartum IUD insertion, however, may increase the risk of problems, such as perforation, pain, and bleeding, which were induced by the exposed copper and the burst release of Cu^{2+} [3, 4] causing cytotoxicity. In order to decrease the limitations of conventional Cu-IUD materials, polymer matrix composites have been developed because of their superiority of controlled release of Cu^{2+} [5–8]. Polyurethanes (PUs) have been widely used for numerous biomedical applications due to their excellent mechanical properties and biocompatibility [9–12]. In this paper, new PU/NC nanocomposites were prepared in situ composite method. In this paper, polyurethane was chosen as the matrix and nanocopper was used as functional filler. The structure, morphology, Cu^{2+} release rate, and water absorption of PU/NC nanocomposites were investigated. PU/NC nanocomposite showed stable Cu^{2+} release behavior by a combination of nanostructure and hydrophilicity modification.

2. Materials and Methods

2.1. Materials and Instruments. Nanocopper was obtained from Shanghai Super Wei Nami Technology Co. Ltd., China; the particle size of nano-copper was 50 nm. Diphenylmethane diisocyanate (MDI) was obtained from Yantai Wanhua Polyurethanes Co. Ltd., China. Polyethylene glycol (PEG) (Mn = 1000) was obtained from Dow Chemical, USA. Polytetramethylene ether glycol (PTMG) was obtained from Mitsubishi Chemical Co., Japan. Both PEG and PTMG were dried under vacuum for 72 h before use. Calcium chloride dihydrate ($CaCl_2$), 1,4-butanediol, glucose, sodium bicarbonate ($NaHCO_3$), and sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$) were obtained from Tianjin Fu Chen Chemical Reagent Factory, China, and used without further purification. Commercial devices (T220c), were obtained from Yantai Family Planning Medicine & Apparatus Co., Ltd., China. UV/Vis absorbance was measured on a UV-4802 UV/Vis Spectrophotometer (Unico Shanghai Instruments Co., Ltd., China). The morphology of the fracture surfaces of the tensile specimens was observed on a scanning electron microscope (SEM) FEI Nova Nano SEM 430 (FEI America Inc.) at an accelerating voltage of 5.0 kV. Fracture surfaces of specimen were sputter-coated with gold prior to their

Table 1: Composition, contact angle, and water sorption of PU/NC nanocomposites.

Samples	PEG	PTMG	MDI	BDO	Copper	Contact angle (°)	Water sorption (%)
PU	40	60	66.7	6.84	0	88.3 ± 0.5	3.7 ± 0.2
P0	0	100	66.7	6.84	5	89.9 ± 0.4	1.1 ± 0.1
P10	10	90	66.7	6.84	5	84.5 ± 0.7	2.7 ± 0.1
P20	20	80	66.7	6.84	5	80.1 ± 0.8	5.0 ± 0.1
P30	30	70	66.7	6.84	5	79.5 ± 0.5	5.4 ± 0.1
P40	40	60	66.7	6.84	5	77.7 ± 1.1	5.8 ± 0.2

Table 2: Composition of simulated uterine solution.

Concentration in water (g/L)					
$NaHCO_3$	$NaH_2PO_4 \cdot 2H_2O$	Glucose	$CaCl_2$	KCl	NaCl
0.25	0.072	0.50	0.167	0.224	4.97

observation. The contact angles of the composites were measured on a Drop Shape Analysis System DSA100 (Krüss GmbH, Germany). ATR-FTIR analysis was conducted using a VERTEX 70 FT-IR (Bruker Optics, Inc., Germany) with an ATR accessory.

2.2. Preparation of PU/Nanocopper Composites. The compositions of the PU/nano-copper composites were show in Table 1. The PEG and PTMG were first mixed at 80°C for 1 h, and then the NC particles were dispersed in the mixture of PEG and PTMG via an ultrasonicator for 1 h at 80°C. Then, the stoichiometric amount of MDI was added to the suspension and reacted at 80°C for 2 h, yielding the prepolyurethane. The whole reaction was carried out under nitrogen with mechanical stirring. The stoichiometric amount of 1,4-butanediol (it was calculated according to the residual amount of NCO) was mixed with the prepolyurethane for 60 s under a violent stirring condition at 110°C. Subsequently, the mixture was cured at 100°C under pressure for 10 h in a metal mould.

2.3. Measurement of Cu^{2+} Release Rate in Simulated Uterine Solutions. Absorbance measurements were employed to measure the Cu^{2+} release rate of PU/NC nanocomposites and T220c in a simulated uterine solution according to the previous literature [13–15]. The composition of the simulated uterine solution is shown in Table 2. The pH value of 6.3 was established by adding dilute hydrochloric acid or sodium hydroxide solution and was adjusted periodically throughout the exposure time. Three specimens of every composite were prepared with a size of 5.0 × 5.0 × 1.0 cm and then suspended into 50 mL simulated uterine solution at 37.0 ± 0.1°C. The amount of released Cu^{2+} of PU/NC nanocomposites and the commercial IUD was determined on the UV-4802 weekly for 3 months.

3. Results and Discussion

3.1. Structure Characterization of PU/NC Nanocomposites. The ATR-FTIR spectroscopy of PU and the P40 are shown in Figure 1. The N–H stretching vibrations bonds were detected at 3150–3500 cm^{-1}. The peaks at 2935 and 2855 cm^{-1} were attributed to CH_2 asymmetric and symmetric stretching vibrations, respectively. The peaks between 1600 and 1800 cm^{-1} indicated the C–O stretching vibrations, and the 1520–1550 cm^{-1} are associated with the urethane N–H bending C–N stretching. The typical peaks of PEG and PTMG were also detected at 1260 cm^{-1} (symmetric CH_3 bending), 1080 cm^{-1} (C–O–C stretching), and 816 cm^{-1} (CH_3 rocking), respectively [16].

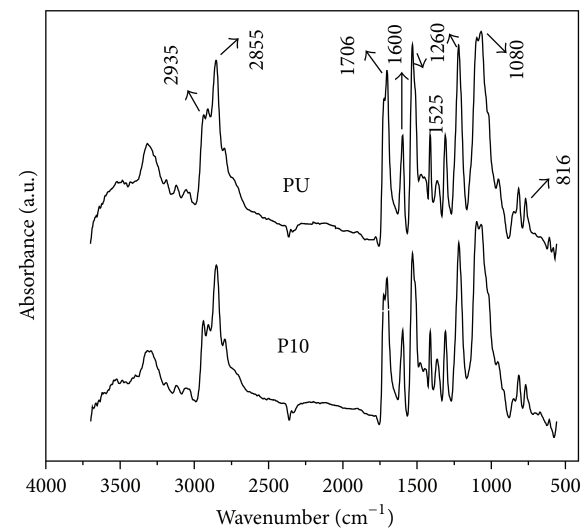


Figure 1: FT-IR spectra of PU and P10.

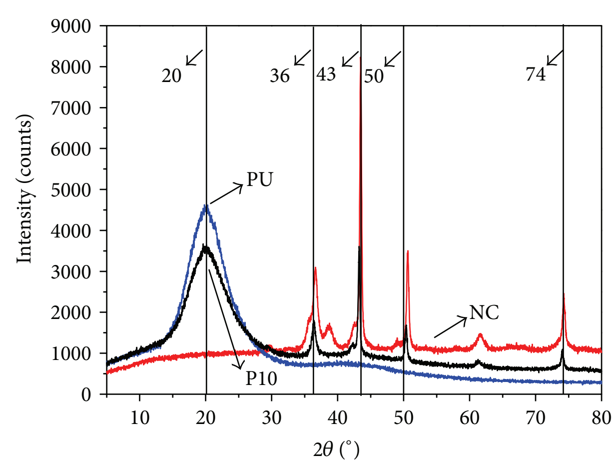


Figure 2: XRD patterns of PU, nano-copper and P10.

Table 3: Average Cu^{2+} release rates of PU/NC nanocomposites for the first month.

Samples	P0	P10	P20	P30	P40
Cu^{2+} release rates (μg/day)	42.2 ± 1.2	46.5 ± 1.1	45.0 ± 1.8	38.7 ± 1.1	60.4 ± 1.6

Table 4: Cu^{2+} release rates of PU/NC nanocomposites at the end of three months.

Samples	P0	P10	P20	P30	P40
Cu^{2+} release rates (μg/day)	33.1 ± 1.0	46.0 ± 1.1	52.4 ± 1.2	65.9 ± 1.3	73.7 ± 1.7

3.2. X-Ray Diffraction Analysis. Figure 2 shows the XRD patterns of PU, nano-copper and P40. PU had broad diffraction peaks in 20° and 42° because there were no microcrystalites in PU samples. In the XRD spectra of the PU/NC nanocomposite, the peaks at 36° belonged to cuprous oxide, and the peaks in 43°, 50°, and 74° belonged to the nano-copper.

3.3. Contact Angle and Water Sorption. Contact angle and water sorption of the PU/nanocopper, nanocomposites are summarized in Table 1. In this research, the hydrophilicity of the nanocomposites increased with the increasing content of the PEG. The contact angle and water sorption of the PU/NC nanocomposites increased with increasing the content of PEG in the soft segments of the composites. This is because the water sorption of the nanocomposites was influenced by the hydrophilicity of the nanocomposites [17, 18]. Therefore, the contact angle and water sorption of nanocomposites increased with increasing the content of the hydrophilic segments, for PEG is more hydrophilic than PTMG.

3.4. Cu^{2+} Release Rate of the PU/NC Nanocomposite. The Cu^{2+} release rates of the composites are shown in Figure 3. The average Cu^{2+} release rates of P0, P10, P20, P30, and P40 are 42.4, 46.5, 45.0, and 60.4 μg/day, respectively. In the first month (as shown in Table 3), there were no burst releases because the nano-copper was wrapped in the polyurethane segments. However, the Cu^{2+} release rates of the PU/NC nanocomposites increased with increase the content of PEG in the soft segment. It may be attributes to the hydrophilicity of the composites. As shown in Figure 3, after six weeks, the release rates of the PU/NC nanocomposites remained relatively stable after six weeks.

The relative Cu^{2+} release rates of P10 and commercial T220c are shown in Figure 4. The Cu^{2+} release rate of T220c showed a burst release in the first two weeks, and the average release rate was about 94 μg/day in the first three months. But the average Cu^{2+} release rate per day in the first three months of P10 was only about 46 μg/day, and there was no initial burst (as shown in Table 4). The average Cu^{2+} release rate was always about 35–55 μg/day. This indicates that the PU/NC nanocomposites have a great potential to replace current commercial Cu-IUD materials.

3.5. Microstructure of the PU/NC Nanocomposites. To investigate the dispersion state of nano-copper in the polyurethane matrix, the tensile fractured surface of P10 was examined by SEM (Figure 5). A uniform dispersion of nano-copper was observed, and no obvious aggregation occurred.

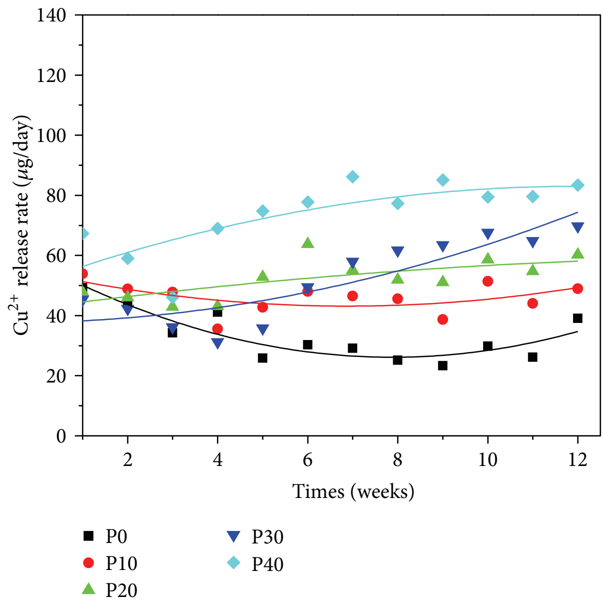


Figure 3: Cu^{2+} release rates of PU/NC nanocomposites.

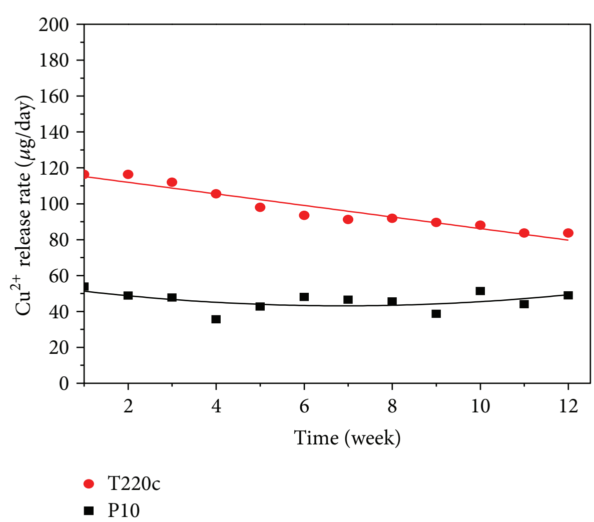
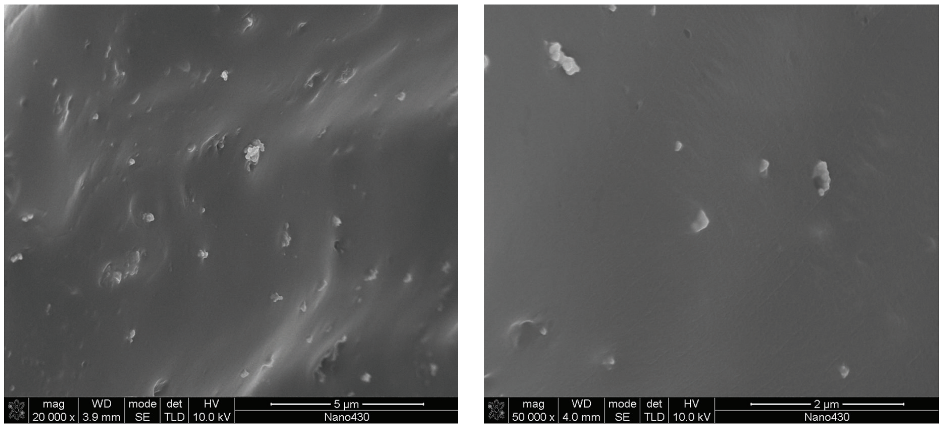


Figure 4: Cu^{2+} release rates of T220c and P10.

4. Conclusions

PU/NC nanocomposites were prepared and used as intrauterine devices. The nano-copper was uniformly dispersed in the nanocomposites. The burst release of the Cu^{2+} could



(a) (b)

FIGURE 5: The SEM image of P10.

be eliminated completely, and the release rates remained relatively stable over three months. These results indicate that the PU/NC nanocomposites have a great potential to replace current commercial intrauterine devices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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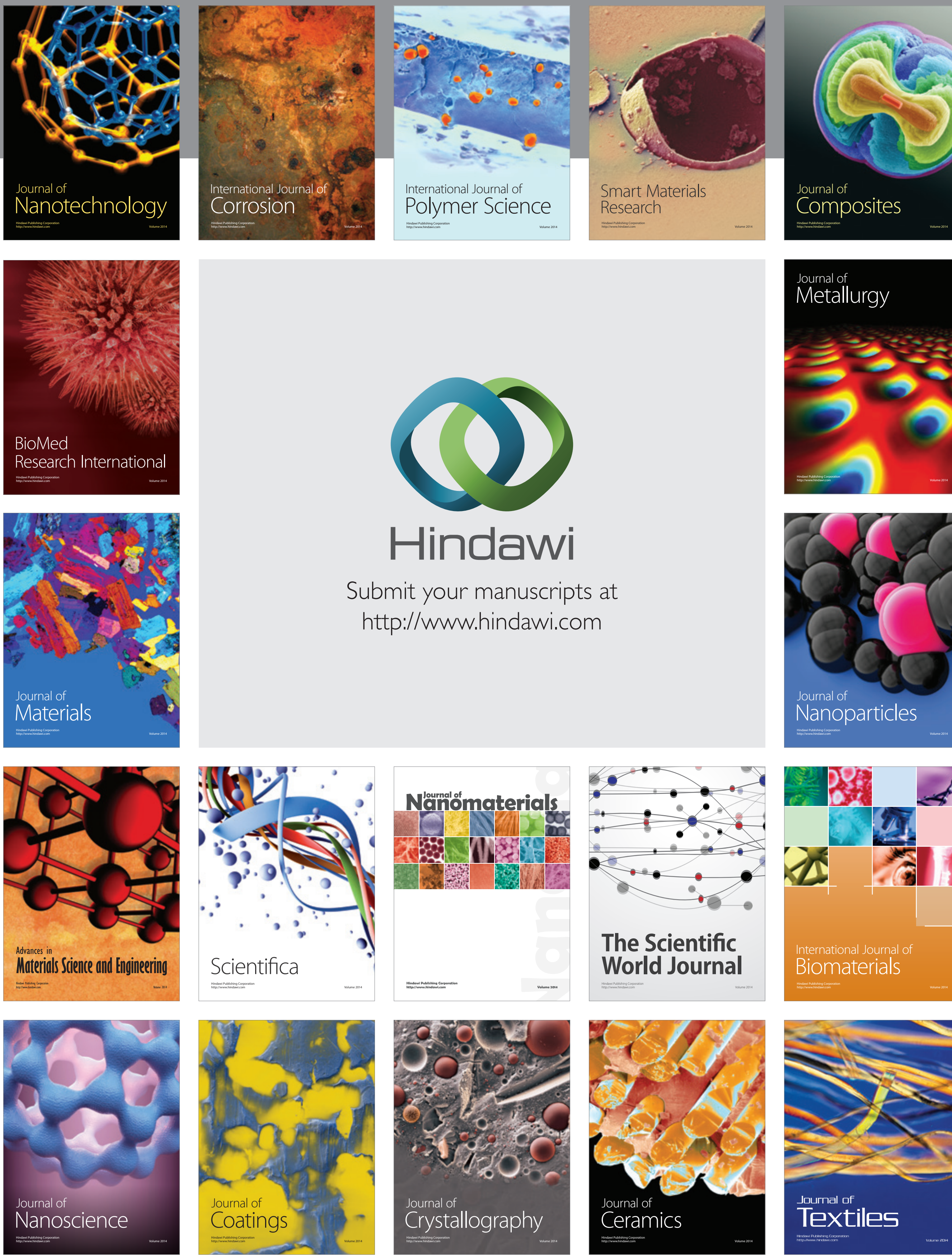
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