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Characterization of Polycaprolactone and Rice Husk Silica Composite (PCL-SiO₂) by E-Spinning to Apply Supporter for Drug Release

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Abstract. Polycaprolactone (PCL) is an interesting material to apply biomedical field owing to its biodegradability and biocompatibility which is suitable for a specific site with longer healing times. Blending the polymer with other materials has degradation property improved with the effective and economic method. This study was conducted to fabricate supporter based on Polycaprolactone and Rice husk silica (PCL-SiO₂) by using electrospinning. Nano-porous silica in the composite was synthesized from rice husk having properties of economic, eco-friendly and high surface area. It drew to enhance the amount of drug loading in the carrier. Electrospinning technique is used to fabricate fibrous component by optimization condition obtained from previous mechanical properties experiments. Release experiment was carried out by the degree of dye absorbance at 544nm by ultraviolet-visible spectroscopy, the RhB in SiO₂ alternative drug for modelling of drug release was released for 1 ~ 20 days at 37°C in phosphate buffer. Furthermore, the Mechanical property was confirmed by DSC, TGA. Morphology and degree of biodegradation were shown as SEM images and EDS.

1. Introduction

Nanoporous Silica have known as a materials to use widely application with high specific surface area such as cosmetics, filler, pharmaceuticals, chromatography which is derived from its hygroscopic and hydrophilic properties. The usage as a drug delivery carrier has increased in medical application because high porous structure property is able to impregnate the active ingredient onto its surface. However the challenge in this experimental is expensive cost of its precursor. In this study, silica extracted from rice husk was used to synthesize nanoporous silica with economical and biocompatible properties.

Polycaprolactone (PCL) is utilized of medical field having biodegradable, but it has weak mechanical properties. In this study, PCL composite with rice husk silica was fabricated as type of nanofiber to overcome the challenge by electronic spinning. By extension, the polymer nanofiber was prepared to apply a material for guided bone regeneration (GBR) with resembling bone structure, which the inorganic component of the nanofiber mimics the hydroxycarbonate-apatite structure while the polymer component mimics the collagen rich extracellular matrix.



2. Experiment

Materials and Pretreatment

Rice husk was obtained from Namhae where is located in southern part of the Republic of Korea. Sodium hydroxide (NaOH) and acetone used in this study are products of DAEJUNG. Hydrochloric acid (HCl) and Polycaprolactone (PCL) were purchased from SAMCHUN chemical and Aldrich respectively. Three steps were conducted to extract silica from rice husk: 1st step was washing rice husk with deionized water to remove dust and drying in an oven. The following step was leaching rich husk with 0.1 M HCl for 2 h at 90 °C then rinsing sufficiently to neutralize. Calcination of clean rice husk to eliminate inorganic impurities remained was the final step. After all these steps, Silica/Carbon powder (rice husk ash; RHA) was obtained

Nano-porous rice husk silica

The RHA was used as raw material to synthesize nano-porous silica. 500mg RHA was added in a 10 ml vial containing 9ml 1.5 M NaOH and boiled in a water bath at 90 °C for 1 h. Conversion from RHA in NaOH to sodium silicate solution was generated during boiling step. The solution was moved to a 50ml beaker and diluted until 1 M concentration with adding deionized water. The diluted sodium silicate solution was quickly titrated up to pH4 by 1.0 M HCl. Steady stirring magnetic bar in the solution was played a role to avoid partial transformation from the silicate sol state to gel upon pH during titration. The mixture was placed in an air oven at 70 °C for 5~8days, which high aging temperature was accelerated reactive silanol group in the gel formation to exist during the process of hydrolysis and condensation. Aged samples were washed with deionized water by centrifuge at 10,000 rpm for 5 min three times then drying in an air oven. The synthesized rice husk silica products were ground to powder and stored in a vacuum desiccator.

PCL-Rice husk silica nanofiber

1.17 g PCL and 20wt% rice husk silica were dissolved in 10 ml acetone at 50 °C for 10 min. The solution was delivered a constant flow rate ($Q = 3$ ml/min) through a metal needle (21 gauge) connected to a high-voltage power supply. The polymer solution was ejected aluminium foil on the surface of the collector from the capillary upon applying a high voltage (18kV) for 40 min. The nanofibers collected on the aluminium foil surface were obtained by peeling with tweezers.

Dye release test

Release test of dye in nano-porous silica was done by the amount of absorbance intensity at 544nm using UV-visible spectroscopy. Prior to conduct release test, a calibration curve of Rhodamine B upon different concentration ($0.21\text{mM} \sim 6.38 \times 10^{-6}$ mM) was constructed by UV absorbance at 544nm of each dye concentration. 50mg nano-porous silica sample was pressed into disks ($1\text{cm} \times 0.3\text{cm}$) using hand pressure machine. Then nano-porous silica tablet sample put into 3ml 3.26×10^{-3} mM Rhodamine B solution and stayed overnight. Amount of dye loading in the tablet samples was checked through the UV absorbance intensity at 544nm of the rest solution by the calibration curve. Each tablet samples with 1 ml Phosphate buffer solution (PBS) were added into 1ml microtube with one side sealing membrane (). The microtubes put into vials containing 20 ml PBS and placed in an incubator at 37°C with 100rpm. A sampling of dye release from silica tablets was carried out on 1, 4, 7, 10 and 15 days. The Samples obtained on each day were dried under freeze-drying and re-dispersed in 5ml DW then analysed with UV-visible spectroscopy.

Polymer degradation test

PCL nanofibers with nano-porous silica samples having a different specific surface area were sized $1\text{cm} \times 1\text{cm}$ and put into vials containing 5ml PBS. The vials were in an incubator at 37°C with 100rpm for 1 ~ 15days. Scanning Electron Microscopy (SEM; Hitachi S-4800S) and Energy Dispersive X-ray (EDX; Horiba EMAX mics) were used to confirm their degradation properties such as change morphology and new elements generated after degradation of PCL.

3. Results and discussion

Nano-porous rice husk silica

Rice husk ash (RHA), raw source to synthesize nanoporous rice husk silica, was obtained through pre-treatments three steps of rice husk (Figure 1).



Figure 1. Images of Rice Husk with each experimental steps

Metallic impurities were eliminated by acidic leaching and calcination process removed maintaining inorganic dust in rice husk to get rice husk ash having high pure silica. Twelve samples were synthesized by several factors such as the amount of RHA, level of pH and aging times, which was named R, P and A implying R to the quantity of RHA, P to pH and A to aging times; e.g. 6R4P7A means 600mg RHA, pH4 and 7 days aging. The reason why factors were chosen was that the specific surface area was likely to be influenced by the level of pH and aging time. Values of specific surface area of the samples were shown in table 1.

Table 1. Specific surface area, pore volume, pore diameter, particle size of nanoporous rice husk silica

Samples	Surface Area _{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
3R4P1A	506.17	0.55	4.38
3R7P5A	240.05	0.87	14.61
3R9P7A	53.02	0.40	30.35
6R9P1A	131.77	0.56	17.16
6R7P7A	111.92	0.59	21.26
6R4P5A	339.60	0.85	10.06
9R7P1A	186.72	0.68	14.62
9R9P5A	35.12	0.20	23.20
9R4P7A	449.92	0.80	7.18
6R4P7A	474.61	0.22	1.89
6R4P6A	756.02	0.49	2.59
6R4P8A	44.9251	0.07	6.91

The nanoporous silica samples were impregnated with Rhodamine B dye to test dye releasing from the samples in aqueous condition at 37°C for several days. Accumulative percentage of dye on releasing time was computed by the trend line equation from the calibration curve of different concentration (1 umol ~ 3.19*10⁻⁵ umol) of Rhodamine B dye shown in figure 2.

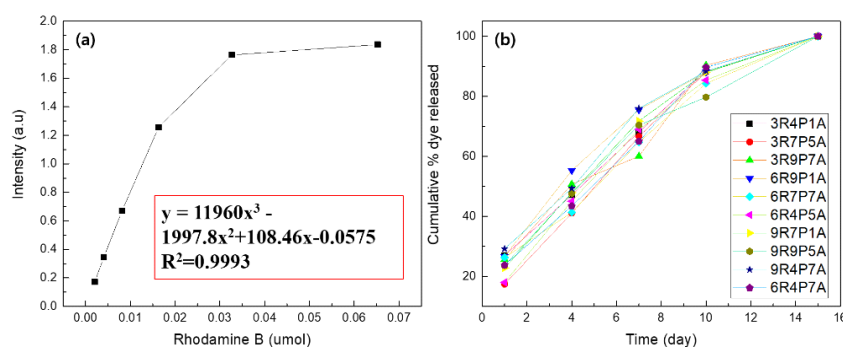


Figure 2. (a) Calibration curve depending on diverse concentration of Rhodamine B dye and trendline equation, (b) cumulative percentage of dye released from nanoporous silica

Silica having large pore size confirmed releasing randomly meanwhile having high specific surface area released the dye steadily and slowly.

Degradation test of PCL-Rice husk silica composite nanofiber

6R4P5A, 6R4P6A, and 6R4P8A were chosen to apply for degradation test of PCL-Rice husk silica nanofiber because this study was aimed to confirm dye release along the specific surface area of silica, which meant aging time was the influencing factor to the value of the specific surface area. The morphology of samples was shown in figure 3.

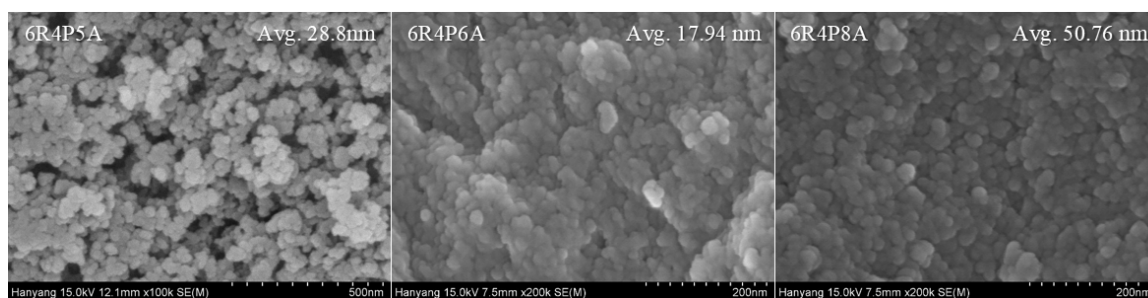


Figure 3. Scanning Electron Microscopy (SEM) images of nano-porous rice husk silica (insert: average particle size)

Particle sizes were ranged from 17.94 nm to 50.76 nm inducing small particles to the high specific surface area and big to a low one. Prior experimental was conducted to confirm optimized dynamic mechanical properties of PCL composites along containing rice husk silica (S_{BET} : 454.845 m^2/g). PCL-20wt% rice husk silica was resulted to be a suitable material for practical application (table 2).

Table 2. Dynamic mechanical properties of PCL-SiO₂ Composites depend on amount of silica containing from the previous study

Sample	T _g (°C)	E' at 30°C (MPa)	E' at 55°C (MPa)
Neat PCL	-46.98	2.38	1.11
PCL-SiO ₂ 10wt%	-52.46	2.43	1.14
PCL-SiO ₂ 20wt%	-54.38	2.48	1.44
PCL-SiO ₂ 30wt%	-49.19	2.16	0.93

The nanofiber samples were analyzed to characterize the other mechanical properties by thermogravimetric analysis (TGA; Dong-il SHIMADZU TGA 50) and differential scanning calorimetry (DSC; TA Q20P). Figure 4 was the result of TGA confirmed PCL-6R4P6A nanofiber with high surface area was rapidly decomposed.

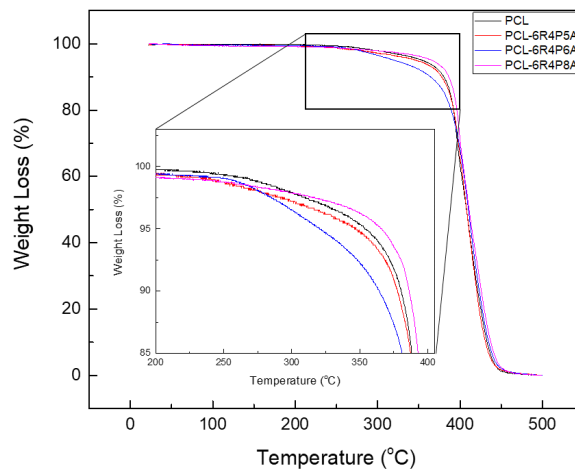


Figure 4. TGA thermal graph of PCL, PCL-6R4P5A, PCL-6R4P6A, PCL-6R4P8A

High specific surface area of nanoporous silica was also verified to induce melting point (T_m) and crystallinity (X_c) to increase shown in figure 5 and table 3 from DSC analysis.

Samples	T_m (°C)	H_m (J/g)	X_c (%)
PCL	59.90	39.13	28.98
PCL-6R4P5A	61.10	24.03	14.24
PCL-6R4P6A	61.64	33.43	19.81
PCL-6R4P8A	59.00	28.27	16.75

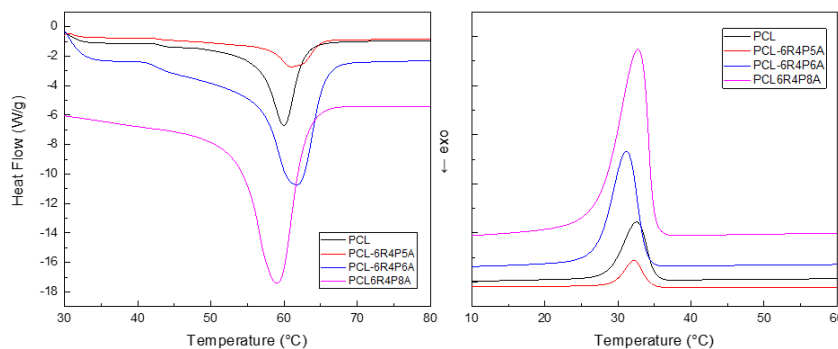


Figure 5. Differential Scanning Calorimetry (DSC) thermal analysis graphs of PCL, PCL-6R4P5A, PCL-6R4P6A, and PCL-6R4P8A

Degradation test of PCL-Rice husk silica nanofiber was progressed in phosphate buffer solution at 37°C along reaction days and the samples were extracted and analyzed to check their morphology change and Ca/P ratio by using SEM and Energy dispersive spectrometer (EDX). Increasing the Ca/P ratio was revealed along reaction days as illustrated in table 4.

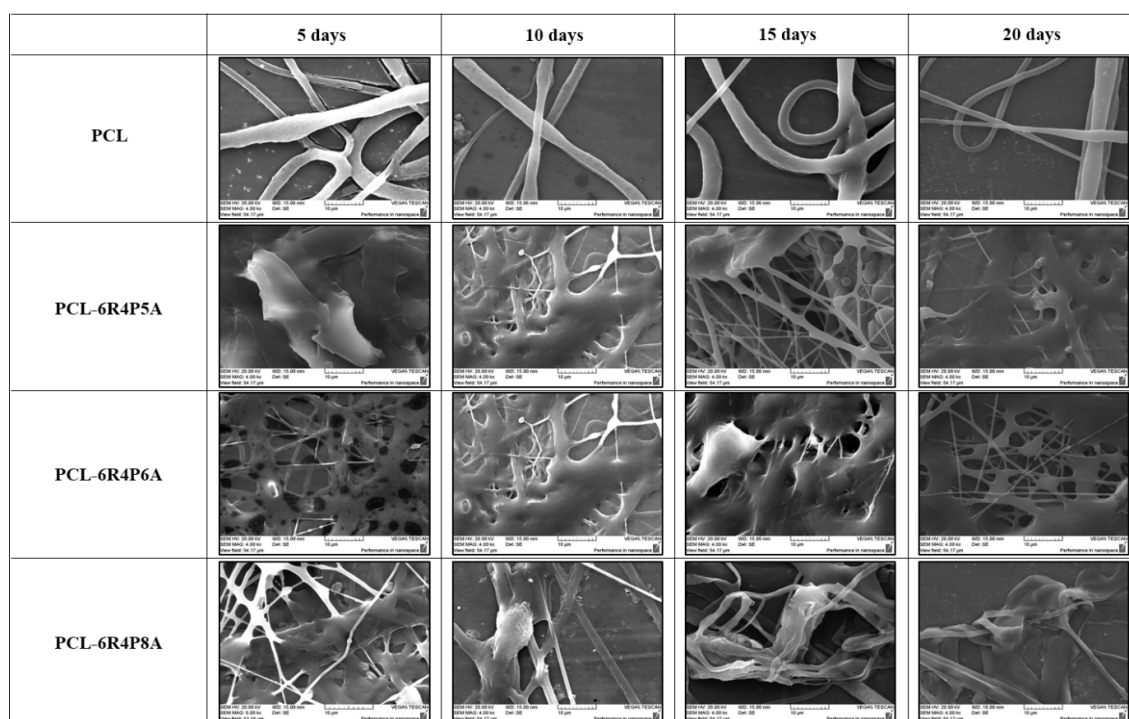


Figure 6. Scanning electron microscopy (SEM) for the surface of PCL-Rice husk silica composites after degradation from 5 to 20 days (scale bar; 10 μ m)

Table 4. Ca/P ratio depending on diverse degradation days of PCL-Silica eco-composites

Ca/P	5 days	10 days	15 days
PCL	0.12	0.18	0.23
PCL-6R4P5A	0.16	0.18	0.59
PCL-6R4P6A	0.15	0.27	0.93
PCL-6R4P8A	0.25	0.16	0.18

The Ca/P ratio of PCL-6R4P6A nanofiber is high after 15 days having large difference comparing the other samples. Nanoporous silica having high specific surface area was indicated to accelerate PCL to decompose itself.

4. Conclusion

Eco friendly nanoporous silica samples having diverse specific surface area were prepared from rice husk which was generated as biomass. The silica samples was impregnated with rhodamine B dye as alternative of real drug and conducted releasing test along times. Rice husk silica having large pore size was released randomly meanwhile high specific surface area silica was constantly done. Subsequently several synthesized nanoporous silica was composited as nanofiber with PCL by using electro spinning. PCL-6R4P6A, nanofiber of high surface area silica with PCL, had increasing melting point and faster degradation comparing with other samples. In the future work, rice husk silica impregnated dye is composed as nanofiber with PCL and conducted dye releasing test along degradation of its polymer.

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