Creation of Superhydrophobic Electrospun Nonwovens Fabricated from Naturally Occurring Poly(Amino Acid) Derivatives

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Creation of superhydrophobic materials bio-inspired by nature fascinates many scientists. One of the most intriguing challenges in this field is the fabrication of these materials using biopolymers from the viewpoint of green chemistry and environmental chemistry. Here, superhydrophobic and biodegradable nonwovens are constructed by electrospinning from a naturally occurring poly(amino acid), poly(γ-glutamic acid) (γ-PGA), modified with a hydrophobic α-amino acid, L-phenylalanine. The contact angle of a water droplet on the materials is 154°, and the droplet remains stuck to the material surface even if it is inverted, clearly indicating a petal-type superhydrophobic property. Biodegradability and post-functionalization of the nonwovens as well as cell adhesion on the superhydrophobic materials are also evaluated. As far as we know, this is the first report on biodegradable materials exhibiting a petal-type superhydrophobicity. The material design and processing shown here can be applied to various bioresources and such functional materials will become a new class of functional materials satisfying some of the requirements in green science.

1. Introduction

Superhydrophobicity seen in a lotus leaf or a rose petal has long fascinated scientists in many fields.[1–6] Inspired by those natural properties, artificial superhydrophobic surfaces have been extensively developed by modifying a surface with chemicals showing low surface free energy and by controlling the topological structure of the surface. Although almost all of them are fabricated from non-degradable components, there are quite a few reports on superhydrophobic materials made of biodegradable polymers.[7–10] As far as we know, Osawa et al. first reported that a micro-patterned poly(ε-caprolactone) surface prepared by a replica method showed superhydrophobic and antibacterial properties.[7] Mano et al. developed superhydrophobic poly(L-lactic acid) films by phase separation and demonstrated poor bacteria adhesion on the materials.[8–10] Indeed, these kinds of superhydrophobic and biodegradable surfaces would not only become a new class of functional materials from the viewpoint of green chemistry and environmental chemistry, but also be intriguing for biomedical and environmental applications.[11–14] Therefore, the use of various biopolymers such as polypeptides and polysaccharides besides polyesters shown above for the preparation of superhydrophobic materials is still of significant interest.

Recent studies have clarified that superhydrophobic surfaces are mainly categorized into two types based on surface properties; a lotus effect surface and a petal effect surface.[6,15,16] The former shows repulsion properties like the beading of water droplets or the water-walking phenomenon of a water strider; while the latter exhibits high adhesive properties like water droplets on a rose petal or a ramie leaf. The abovementioned biodegradable and superhydrophobic polyesters showed a water-repellent property characteristic of a lotus surface, which motivated us to prepare biodegradable and petal-type superhydrophobic materials. Guo recently reported that the rear face of the ramie leaf and the surface of Chinese watermelon show petal-type superhydrophobicity and have simple, unitary micro-line structures.[6,17] Inspired by these structures seen in nature, in this study we focused on electrospinning which is a simple and versatile technique for producing amazingly long fibers with micro- to nanometer-sized diameters from various types of synthetic and bio-based polymers.[18–20] Many superhydrophobic nonwovens with rough surface structures have been developed by electrospinning, but there is no report on the preparation of superhydrophobic nonwovens composed of only bioresources. Nonwovens prepared by such a simple and versatile technology would be meaningful in industrial applications.

Herein, we report for the first time the preparation of biodegradable electrospun nonwovens with a petal-type superhydrophobicity. Poly(γ-glutamic acid) (γ-PGA) is a naturally occurring poly(amino acid) with good biodegradability and biocompatibility,[21] and γ-PGA-based materials have been employed in biomedical, cosmetic, and superabsorbent material fields.[22,23] We have reported on various γ-PGA materials, such as nanoparticles,[24] hydrogels,[25,26] and fibers.[27] In the course of

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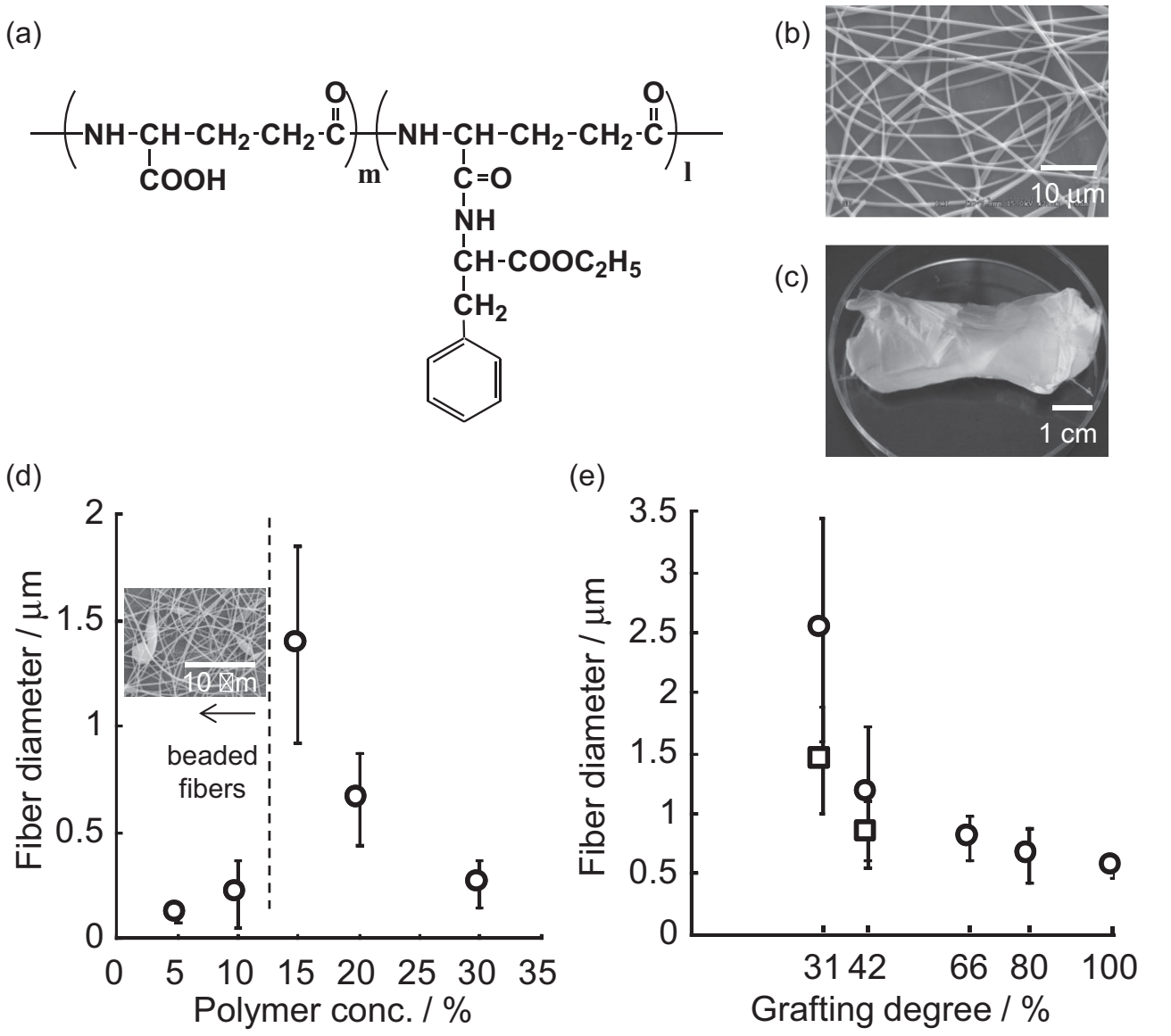

Figure 1. a) Chemical structure of γ-PGA-Phe. b,c) SEM image and photograph of electrospun fibers and nonwovens from 20% γ-PGA-Phe-80 solution in HFIP. d) The effect of polymer concentration to the diameter of electrospun γ-PGA-Phe-80 fibers. Fiber diameter was calculated from SEM images of three different samples (n = 30). At the concentration of less than 10%, beaded fibers were formed (inset). e) The effect of the grafting degree of γ-PGA-Phe to fiber diameter with a flow rate of 0.50 (indicated by ○) or 0.25 mL/h (□). Polymer concentration was 20%.

these studies, we found that γ-PGA modified with L-phenylalanine ethylester (γ-PGA-Phe, **Figure 1**a) can be dissolved into 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), which is well known as a powerful solvent for electrospinning. Other advantages are that γ-PGA-Phe has good biocompatibility and biodegradability and can be produced at gram scale via simple chemical modification of γ-PGA.[22,24] A series of γ-PGA-Phe with different grafting degrees were synthesized according to a previous report,[24] and the γ-PGA-Phe/HFIP solutions were electrospun for fabrication of the biodegradable nonwovens. The contact angle (CA) of a water droplet on the nonwovens was over 150°, and the droplet remained stuck even after it was inverted. These results indicate that the biodegradable nonwovens show a petal-type superhydrophobicity, which have not been reported before. To further explore this field, cell adhesion on the materials was also investigated. We believe that the material design and processing is applicable to different biopolymers and is important for academic researches as well as for practical applications. Furthermore, such functional materials would satisfy some of the requirements in green chemistry and environmental chemistry.

2. Results and Discussion

2.1. Electrospinning of γ-PGA-Phe

According to a previous report,[24] a series of γ-PGA-Phe with 18, 31, 42, 66, 80, and almost 100% grafting degrees (abbreviated

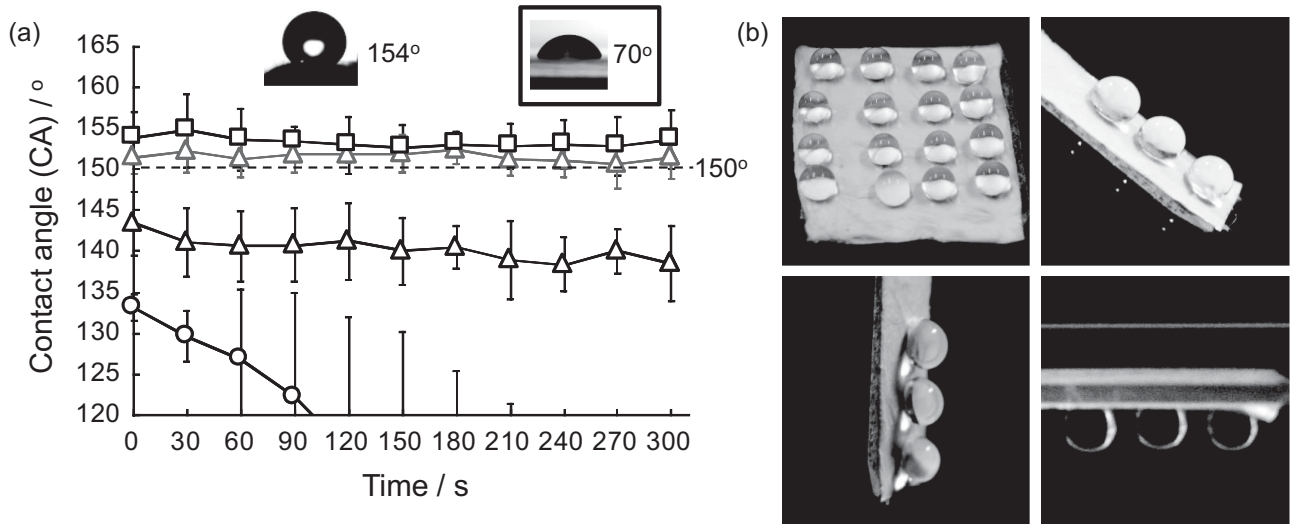

Figure 2. a) Time dependency of surface wettability of γ-PGA-Phe-66 (○), -80 (Δ), and -100 nonwovens (□) ($n = 10$). A red line shows the case of acidic water droplet (pH 3). The inset surronded by a black box shows the CA of water droplet on the γ-PGA-Phe-100 cast-film. b) Strong adhesion of water droplet onto γ-PGA-Phe-100 nonwovens with different tilt angles: 0, 45, 90, and 180°.

as γ-PGA-Phe-18, -31, -42, -66, -80, and -100) were synthesized, and γ-PGA-Phe with more than 30% substituents were used for the following electrospinning due to good solubility in HFIP (Table S1).

Electrospinning of the γ-PGA-Phe solutions onto an aluminum substrate was examined. A representative experiment was performed by using 20% (w/v) γ-PGA-Phe-80 solution with an applied voltage of 20 kV, collection distance of 20 cm, and a flow rate of 0.50 mL/hour. The formed fibers were homogeneous and 660 ± 220 nm in diameter (Figure 1b), and bulk nonwovens could be easily peeled off from the substrates after 2 h electrospinning (Figure 1c). At a concentration of more than 15%, the diameter of γ-PGA-Phe-80 fibers decreased with increasing polymer concentration (Figure 1d). This result seems to be different from a general tendency in electrospinning. The reason remains unclear, but jet instabilities during electrospinning may cause thinning which can lower the electrostatic interaction energy between fibers.[28] On the other hand, as the concentration decreased below 15%, finer fibers containing beads were produced. Similar results were observed for all other γ-PGA-Phe with different Phe grafting degrees, and the diameter of the fibers obtained decreased with increasing Phe degrees (Figure 1e and Supporting Information Figure S1a–e), which was probably caused by better solubility of γ-PGA-Phe with larger grafting degrees in HFIP (Figure S2, Supporting Information). A slower flow rate was required to generate homogeneous fibers for γ-PGA-Phe-31 and -42, due to their lower solubility in HFIP (Figure 1e and Supporting Information Figure S1e,f,S2). Water solubility of the nonwovens was similar to that of the original polymers, and γ-PGA-Phe-66, –80, and –100 nonwovens were stable in water for over 1 month. FT-IR spectra did not show any difference between the original polymers and the obtained fibers, suggesting that the chemical structure of the polymers in the fibers was close to the original structures (Figure S3, Supporting Information). In addition, X-ray diffraction (XRD) measurement of these fibers was performed (Figure S4, Supporting Information), since electrospinning often increases fiber crystallinity,[29] but any distinct diffraction was not observed, indicating that the molecular structure of the fibers formed are amorphous, similar to that of the self-assembled γ-PGA-Phe nanofibrils reported previously.[30] This may be because γ-PGA are composed of random sequences of L-/D-residues.

2.2. Wettability of γ-PGA-Phe Nonwovens

Surface wettability of water-insoluble γ-PGA-Phe-66, –80, and –100 nonwovens was evaluated by measuring the CA of a 1 μL water droplet on a nonwoven fixed onto a glass plate over 5 min. The initial CA increased with increasing Phe units, and it is surprising that the value of γ-PGA-Phe-100 nonwovens was 154°, suggesting superhydrophobicity (**Figure 2**a). γ-PGA-Phe-66 nonwovens with the least grafting degree showed the lowest hydrophobicity of the three and the CA reduced as time went by. In contrast, the droplets on the others were very stable and kept their shapes even after 30 min incubation. The change in wettability was also monitored by controlling protonation/deprotonation of the carboxylic groups remaining in the polymers. The γ-PGA-Phe-66 nonwovens had significantly improved hydrophobicity when kept in acidic conditions for over 5 min (Figure S5a, Supporting Information), and γ-PGA-Phe-80 nonwovens became superhydrophobic under acidic conditions (Figure 2a). Such results clearly show the increased hydrophobicity by protonation of the carboxylic groups in the polymers. On the other hand, the CA decrement was clearly observed for all samples when alkaline droplets were used (Figure S5b, Supporting Information), indicating that the nonwovens became more hydrophilic by deprotonation of the carboxylic groups in the polymers and even the γ-PGA-Phe-100 samples contained carboxylic groups. Surface root-mean square (RMS) roughness of these samples was compared with a 3D laser scanning

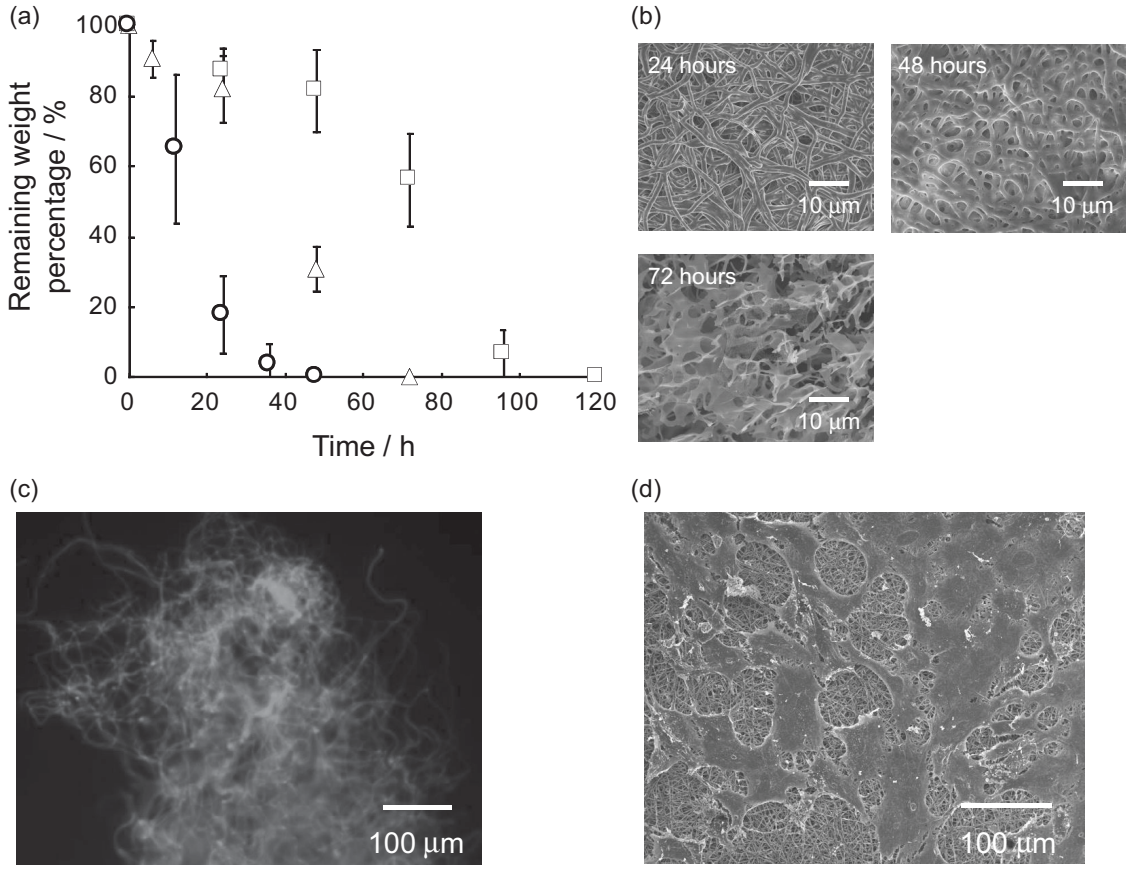

Figure 3. a) Weight remaining of γ-PGA-Phe-66 (○), -80 (Δ), and -100 (□) in $NaHPO_4$/NaOH solution (pH 12) at 37 °C. b) Morphological changes of biodegraded γ-PGA-Phe-100 nonwovens. c) Confocal fluorescent image of γ-PGA-Phe-80 nonwovens modified with Alexa Fluor 488 dye. d) SEM image of human endothelial cells adhered on γ-PGA-Phe-100 nonwovens after 2 days culture.

microscope, but a big difference was not observed (Figure S6, Supporting Information). The CA on the γ-PGA-Phe-100 cast-films prepared as a control was approximately 70°, much smaller than that on the corresponding nonwovens. The surface structures were much smoother and the RMS roughness was about 2.0 μm (Figure 2 inset and Supporting Information Figure S7). Furthermore, water droplets put on the nonwovens were stably adhered and stayed still on the surface, even if it was turned over (Figure 2b). It is known that this phenomenon is characteristic of a petal-type superhydrophobic surface. From these results, we concluded that the surface wettability resulted from the rough, fibrous morphology as well as from the hydrophobic difference at the molecular level.

2.3. Chemical and Biological Properties of γ-PGA-Phe Nonwovens

It is generally thought that the beading of a water droplet on a superhydrophobic surface is caused by the air present between the surface and the droplet.[15,16] Different from previous water-repellent materials based on polyesters,[7–10] the biodegradability of the γ-PGA-Phe nonwovens can be investigated because of the adhesion of water droplets on the nonwovens. Biodegradability of the electrospun nonwovens was investigated by forcibly immersing approximately 4 mg of the nonwovens in $NaHPO_4$/NaOH buffer solution (pH 12) at 37 °C (**Figure 3**a). All nonwovens were gradually degraded with increasing immersion time and finally distinguished. As the grafting degree increased, the degradation proceeded slower, indicating that hydration of the materials is a key step in biodegradation. The morphological change of the γ-PGA-Phe-100 nonwovens was observed by SEM (Figure 3b). Although the fibrous morphology was clearly maintained after 24 h, aggregation and fusion of the fibers were observed after 48 h, and the original structure was completely destroyed after 72 h. Such a biodegradable property might be a disadvantage in the creation of superhydrophobic materials with the long-term stability and toughness, but we believe that this material concept would be beneficial for biomedical and environmental applications of superhydrophobic materials.

A post-modifiable property would be promising for superhydrophobic surfaces. Because γ-PGA-Phe nonwovens have chemically modifiable functional groups, fluorescent molecules could be conjugated to γ-PGA-Phe-80 nonwovens via carbodiimide chemistry. As shown in Figure 3c, fluorescently labeled nonwovens could be obtained, suggesting successful chemical modification. This manipulation may allow the on-demand surface modification of superhydrophobic materials.

One of the hottest topics in the study of superhydrophobic materials is bacteria and cell adhesion on superhydrophobic

surfaces.[10,31] However, the adhesion properties of bacteria and cells would not be related to the type of superhydrophobicity (petal or lotus) and much more data is required to address this issue. Thus, various cells were cultured on the γ-PGA-Phe-100 nonwovens, such as human endothelial cells, human fibroblast cells, mouse C2C12 myoblast cells, and mouse RAW264 macrophages (Figure 3d and Supporting Information Figure S8). All the cells used adhered and all the cells, except for the macrophages, grew and proliferated over time in culture. We hypothesize that a petal-type superhydrophobic surface allows direct contact of proteins and cells mediated by water, but the mechanism remains unclear because previous work showed cell adhesion on a lotus-type superhydrophobic surface.[32] Detailed studies on cell culture are now in progress.

As shown above, biodegradable and superhydrophobic nonwovens were successfully created by electrospinning of poly(amino acid) derivatives. In the biomedical and tissue engineering fields, essential properties such as biocompatibility, biodegradability, protein adsorption, cell adherence, and blood compatibility of biomedical materials (gauzes, catheters, and so on) are controlled by the topology and wetting properties of a given material's surface. The polymer used in this study, γ-PGA-Phe, will provide a variety of materials with different surface wetting properties simply by tuning surface topology (e.g. films, nonwovens) depending on the target and field of the applications.

3. Conclusion

In conclusion, we prepared biodegradable nonwovens exhibiting a petal-type superhydrophobicity made only of bioresources. The nonwovens could be prepared by simple electrospinning of γ-PGA modified with a hydrophobic amino acid. The wetting property was easily tuned depending on the amount of hydrophobic moieties and the remaining functional groups can be employed for on-demand chemical modifications. We believe that the material design and processing can be applied to various biodegradable polymers and is of significant importance for academic research as well as for practical applications. Furthermore, such functional materials would satisfy some of the requirements in green chemistry and environmental chemistry.

4. Experimental Section

Materials: All chemicals were used as received. γ-PGA (Mw = 483 000, D-Glu/L-Glu = 70/30) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) were purchased from Wako Pure Chemical Industries (Osaka, Japan). L-phenylalanine ethylester (Phe) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were obtained from Sigma (St. Louis MO, USA). Alexa Fluor 488 cadaverin sodium salt was purchased from Molecular Probes (USA).

Synthesis of γ-PGA-Phe with Different Grafting Gegrees: A series of γ-PGA-Phe were synthesized as previously described.[24] Briefly, γ-PGA (10 unit mmol) was reacted with hydrophobic Phe (10 or 20 mmol) in the presence of EDC (2.5, 5, 7.5, 10, or 20 mmol) in 100 mM sodium hydrogen carbonate ($NaHCO_3$) aqueous solution for 24 h at room temperature. The purified γ-PGA-Phe polymers were then characterized by ^{1}H NMR spectroscopy. The grafting degree of Phe units was determined from the integral intensity ratio of the methylene peaks of γ-PGA to the phenyl group peaks of Phe. γ-PGA-Phe with 18, 31, 42, 66, 80, and almost 100 Phe groups per 100 glutamic acid units of γ-PGA (γ-PGA-Phe-18, -31, -42, -66, -80, and -100) were prepared. Detailed preparation condition, grafting degrees of the obtained polymers, and their solubility in water and HFIP are summarized into Supporting Information Table S1.

Electrospinning of γ-PGA-Phe: The synthesized γ-PGA-Phe polymers were dissolved in HFIP under magnetic stirring at room temperature (r.t.) at the concentration of 5, 10, 15, 20, and 30% (w/v) for γ-PGA-Phe-80 and 20% (w/v) for the others. Electrospinning was performed by pumping the polymer solution through a single-use blunt end cannula with a diameter of 21 gauge at different flow rates (0.25 and 0.50 ml/hour). A high voltage power supply (Bertan Series 205B, New York, USA) applied high voltage of 20 kV to the polymer solution. The collection distance between the cannula and the target was fixed at 20 cm. Aluminium foil (10 cm × 10 cm) was used as a collecting target. The morphologies of the obtained fibers were observed by scanning electron microscopy (SEM) (Hitachi S3000 N, Germany).

Measurement of CA of Water on γ-PGA-Phe Nonwovens: The 20% of γ-PGA-Phe-66, -80, and -100 solutions in HFIP were electrospun for 2 h to obtain the nonwovens. CA was measured by DropMaster500 Kyowa Interface Co., Ltd. A 1 μL of water droplet was put on the nonwovens and temporal change of CA was measured every 30 s over 5 min. For evaluating the effect of the droplet pH to CA, 0.001 M hydrochloric acid (HCl) and 0.01 M sodium hydroxide (NaOH) solutions were used.

Investigation on Surface Roughness of γ-PGA-Phe Nonwovens: RMS roughness was measured by COLOR 3D Laser Scanning Microscope UK-9700 (KEYENCE, Japan) and a supplied program, UK-H1A1 Analyzer.

Evaluation of Biodegradability of γ-PGA-Phe Nonwovens: Approximately 4 mg of the γ-PGA-Phe-66, -80, and -100 nonwovens were forcibly immersed into 0.1 M $NaHPO_4$/NaOH buffer solution (pH 12). After the prescribed incubation times, the remaining solids were collected and weighed. Morphological changes at the prescribed degradation times were observed with field emission SEM (FE-SEM) (JEOL 6701F, Japan).

Chemical Modification of γ-PGA-Phe-80 Nonwovens with Fluorescent Molecules: Approximately 4 mg of the γ-PGA-Phe-80 nonwovens were forcibly immersed in 5 mL of ultrapure water. 10 mg of EDC and 100 μg of Alexa Fluor 488 cadaverine sodium salt were added and reacted overnight. Then, the sample was taken out, extensively washed with ultrapure water, and dried in vacuum. The obtained nonwovens exhibited superhydrophobic properties at acidic pH, similar to the nonwovens before the modification. The fluorescence image of the nonwovens was taken with Olympus Disk Scan System DSU-IX80-SET (Japan).

Cell Culture on γ-PGA-Phe Nonwovens: Approximately 4 mg of the γ-PGA-Phe-80 and –100 nonwovens were forcibly immersed in 70% ethanol and washed with phosphate buffered saline (PBS). A total of 1×10^5 human fibroblast cells (passage 10, Sanko), human umbilical vein endothelial cells (passage 5, CAMBREX), and mouse C2C12 myoblast cells (passage 11, kindly donated by Prof. Y. Sawa in Osaka University) were seeded onto the nonwovens and incubated for 24 or 72 h. Fibroblasts and myoblasts were cultured in Dulbecco's modified Eagle medium (DMEM) containing 10% fetal bovine serum (FBS). Endothelial cells were cultured in endothelial basal medium-2 (EBM-2; CAMBREX, USA) containing hFGF-B, vascular endothelial growth factor (VEGF), R3-IGF-1 (IGF-1 = insulin-like growth factor 1), ascorbic acid, FBS, hEGF, and GA-1000. The samples were then washed in PBS and fixed with 10% formalin aqueous solution for 15 min. The fixed gels were immersed alternatively in ethanol (50, 60, 70, 80, 90, and 99.5%) and tert-butyl alcohol. After freeze-drying and osmium coating, the cells adhered on the nonwovens were observed with FE-SEM.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988.
[2] A. B. D. Cassie, *Discuss. Faraday Soc.* **1948**, *53*, 1466.
[3] L. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 5998.
[4] X. Feng, L. Jiang, *Adv. Mater.* **2006**, *18*, 3063.
[5] P. Roach, N. J. Shirtcliffe, M. I. Newton, *Soft Matter* **2008**, *4*, 224.
[6] Z. Guo, W. Liu, B. Su, *J. Colloid Interface Sci.* **2011**, *353*, 335.
[7] S. Osawa, M. Yabe, M. Miyamura, K. Mizuno, *Polymer* **2006**, *47*, 3711.
[8] J. Shi, N. M. Alves, J. F. Mano, *Bioinsp. Biomin.* **2008**, *3*, 034003.
[9] W. Song, D. D. Veiga, C. A. Custodio, J. F. Mano, *Adv. Mater.* **2009**, *21*, 1830.
[10] N. M. Alves, J. Shi, E. Oramas, J. L. Santos, H. Tomas, J. F. Mano, *J. Biomed. Mater. Res. Part A* **2009**, *91A*, 480.
[11] Y. Ikada, H. Tujii, *Macromol. Rapid Commun.* **2000**, *21*, 117.
[12] R. A. Gross, B. Kalra, *Science* **2002**, *297*, 803.
[13] T. Kaneko, T. H. Thi, D. J. Shi, M. Akashi, *Nat. Mater.* **2006**, *5*, 966.
[14] S.-W. Hwang, G. Park, H. Cheng, J.-K. Song, S.-K. Kang, L. Yin, J.-H. Kim, F. G. Omenetto, Y. Huang, K.-M. Lee, J. A. Rogers, *Adv. Mater.* **2014**, *26*, 1992.
[15] S. Wang, L. Jiang, *Adv. Mater.* **2007**, *19*, 3423.
[16] L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia, L. Jiang, *Langmuir* **2008**, *24*, 4114.
[17] Z. G. Guo, W. M. Liu, *Plant Sci.* **2007**, *172*, 1103.
[18] D. Li, Y. Xia, *Adv. Mater.* **2004**, *16*, 1151.
[19] C. Y. Xu, R. Inai, M. Kotaki, S. Ramakrishna, *Biomaterials* **2004**, *25*, 877.
[20] X. Li, C. Wang, Y. Wei, *Small* **2009**, *5*, 2349.
[21] H. Kubota, T. Matsunobu, K. Uotani, H. Takebe, A. Satoh, T. Tanaka, M. Taniguchi, *Biosci. Biotechnol. Biochem.* **1993**, *57*, 1212.
[22] T. Akagi, M. Baba, M. Akashi, *Polymer* **2007**, *48*, 6729.
[23] M. J. Zohuriaan-Mehr, A. Pourjavadi, H. Salimi, M. Kurdtabar, *Polym. Adv. Technol.* **2009**, *20*, 655.
[24] M. Matsusaki, K. Hiwatari, M. Higashi, T. Kaneko, M. Akashi, *Chem. Lett.* **2004**, *33*, 398.
[25] H. Yoshida, M. Matsusaki, M. Akashi, *Adv. Funct. Mater.* **2009**, *19*, 1001.
[26] H. Yoshida, M. Matsusaki, M. Akashi, *Adv. Funct. Mater.* **2013**, *23*, 1736.
[27] H. Yoshida, K. Klinkhammer, M. Matsusaki, M. Möller, D. Klee, M. Akashi, *Macromol. Biosci.* **2009**, *9*, 568.
[28] D. H. Reneker, A. L. Yarin, E. Zussman, H. Xu, *Adv. Polym. Mech.* **2007**, *41*, 43.
[29] T. Kongkhlang, K. Tashiro, M. Kotaki, S. Chirachanchai, *J. Am. Chem. Soc.* **2008**, *130*, 15460.
[30] T. Kaneko, M. Higashi, M. Matsusaki, T. Akagi, M. Akashi, *Chem. Mater.* **2005**, *17*, 2484.
[31] H. Zhu, Z. Guo, W. Liu, *Chem. Commun.* **2014**, *50*, 3900.
[32] K. J. Cha, K. Park, S. Lee, *Macromol. Biosci.* **2011**, *11*, 1357.