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Preparation of super-hydrophobic surface on biodegradable polymer by transcribing microscopic pattern of water-repellent leaf

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Abstract

Super-hydrophobic surface has been prepared onto biodegradable polymer by a combination of transcribing microscopic structure of a water-repellent leaf and a chemical treatment. An aroid leaf has been chosen for the preparation of the super-hydrophobic surface since the leaf has concavity microscopic structure, which is easy to handle for a material use. The microscopic pattern was transcribed onto poly(ε-caprolactone) (PCL) sheet by using replica method, then it was further treated by soaking in a mixture of acetone/methanol solution. The resultant PCL having the microscopic concavity pattern showed high water contact angle of 148° and also showed antibacterial property for filamentous fungi.

Keywords: Biodegradable polymer; Water repellency; Poly(ε-caprolactone)

1. Introduction

Water repellency is widely used in many industrial products, such as umbrella, mackintosh, sports wear, flying pan, and self-cleaning glass [1–3]. High water-repellent surfaces showing water contact angle larger than 120° have been obtained by controlling surface roughness and lowering the surface energy [4–7]. Introducing the water-repellent surface onto biodegradable polymer must result in other new functions. For examples, water repellency prevents hydrolysis of polyester, which can be applied to control the degradation rate of the polymer, e.g. no degradation in the use then it degrades faster after the waste. The antibacterial property may also be obtained by the water repellency on the biodegradable polymer surface.

Tsujii et al. have paid special attention to the geometrical structure of solid surfaces and found the excellent effectiveness of fractal structure on the wettability [8,9]. They showed that super water-repellent surfaces showing contact angles over 170° for water droplets have been made of alkylketene dimmer (a kind of wax). The contact angle of rough solid surface is usually explained by the following Wenzel equation [10].

$$\cos\theta' = r\cos\theta \qquad (1)$$

where θ' and θ are the contact angles on rough and flat solid surfaces, respectively, and r is a roughness factor, which is defined as the ratio of actual surface area of a rough surface to the flat one. Eq. (1) indicates that rough surface will be more water-repellent when θ is greater than 90°. Unfortunately, contact angles of most biodegradable polymers are less than 90°, because their chemical structures consist of hydrophilic ester bonds. Therefore, a special structure might be needed for the preparation of water-repellent biodegradable polymer.

It is well known that a surface of lotus leaf has micro-scale roughness, resulting in water contact angle up to 170° because air is trapped under the droplets and the wax crystals at the external plant surface minimizes the contact area. Other natural leaves such as aroid, eucalyptus, and willy also show high water repellency, even though their micro-scale patterns are much different from that of lotus. For these leaves, Cassie equation [11] can be applied to explain such high contact [12].

$$\cos\theta' = \phi\cos\theta_1 + (1-\phi)\cos\theta_2 \qquad (2)$$

where θ_1 is contact angle of solid surface of flat leaf and θ_2 is that of air (180°), and ϕ the ratio of actual surface area of the leaf to the area of air under the water droplet. According to Eq. (2), the leaf like structure might be result in hydrophobic surface even on biodegradable polymer, if ϕ is sufficient small, i.e. the structure can trap sufficient air between water droplet and the surface. Recently, Erbil et al. [13] have reported a simple method for forming a super-hydrophobic coating using polypropylene and a suitable selection of solvents and

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temperature to control the surface roughness. The method can be applied to a variety of polymer surfaces.

In this study, we attempted to prepare the super-hydrophobic surface on biodegradable polymer by a combination of transcribing the microscopic pattern of a water-repellent leaf and the solvent treatment. The resultant biodegradable polymer surface showed high water contact angle of c.150° and also showed an antibacterial property.

2. Experimental

The micro-scale pattern of water-repellent leaf was transcribed onto poly(ε-caprolactone) (PCL) (Daicel Chemical Co. Ltd, CELGREEN PH-7) by using a replica method. Commercially available gel type silicon sealer was poured onto the leaf at room temperature. After the silicon sealer was completely solidified (it became to be rubber sheet), the leaf was pealed off from the silicon rubber. The negative-pattern of the leaf was transcribed onto the silicon rubber. Then, PCL/dioxane solution was poured on the silicon rubber and dried for over 24 h. The micro-pattern of the leaf could be transcribed on PCL sheet by pealing off the silicon rubber. Then the transcribed PCL was immersed in acetone/methanol mixture solution within several minutes.

The water contact angles of the leaf and of the transcribed PCL surface were measured by using contact angle apparatus (FACE contact angle apparatus CA-D type, Kyowa Interface Science Co. Ltd). The micro-scale pattern of the leaf and the transcribed PCL were observed by scanning electron microscope (SEM). The roughness of the sample was evaluated by 10-points mean average method.

3. Results and discussion

Table 1 shows water contact angles of several leaves having water repellency. Lotus has the highest contact angle of 149°, and other leaves show also high contact angles over c. 120°. The microscopic structures of those leaves were much different as shown in Fig. 1. Lotus has spiniferous pattern, which is suitable structure to form air pockets between droplet and the surface [14,15]. However, the spines on the surface might be easily spoiled and is also difficult to handle it for a material use. On the other hand, aroid has concavity-pattern, which seems to be suitable to maintain the pattern in the use. Willy has a radial pattern, however, the structure is too complex to transcribe the pattern. Among the structures, we have chosen a structure of aroid leaf for preparing super-hydrophobic surface on PCL sheet since it has high water contact angle and the concavity-pattern is thought to be enough handle for a material use.

Table 1
Contact angles of water-repellent natural leaves

Sample leaves	Contact angle (°)
Leaf of an aroid	146
Leaf of a eucalyptus	119
Leaf of a lotus	149
Leaf of a willy	121

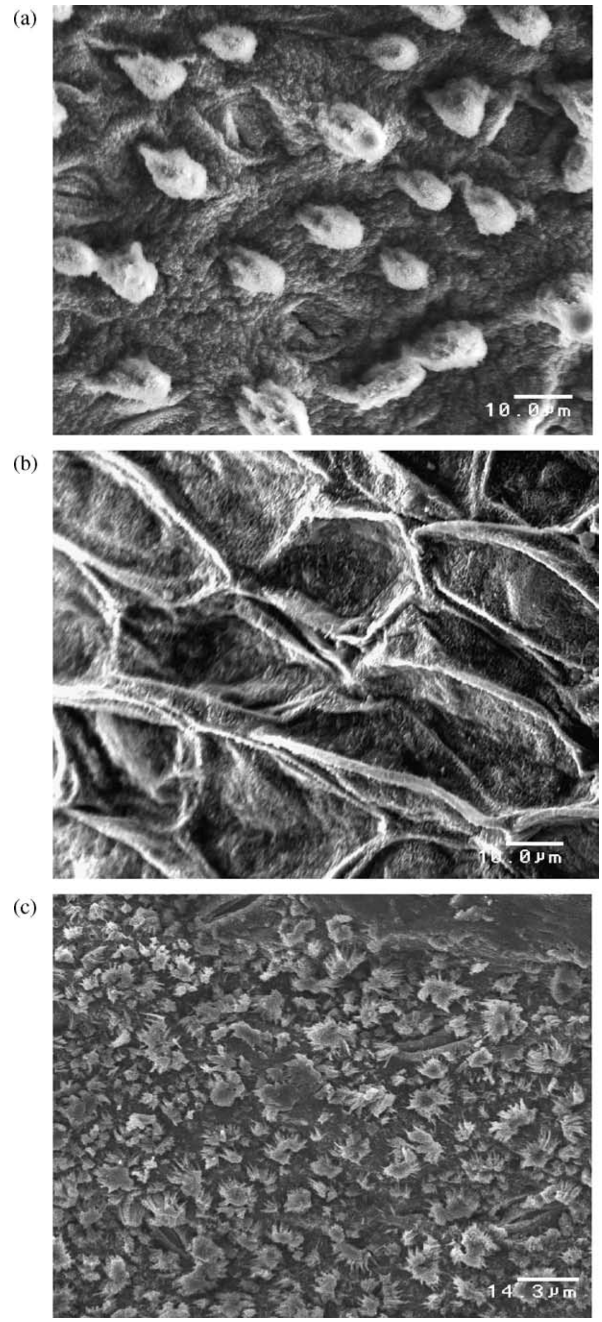

Fig. 1. Scanning electron micro photographs of typical patterns of lotus (a), aroid (b), and willy (c) leaves.

Fig. 2 shows typical SEM photograph of transcribed surface of resultant PCL sheet. The concavity-pattern of aroid was transcribed onto PCL surface in order of c. 28 μm scale. However, sub-micrometer ordered asperity pattern was not clearly transcribed. The transcribed PCL surface had a water contact angle of 107°, which was 35° higher than that of un-transcribed original flat PCL sheet (contact angle of 72°). The flat surface was made on glass plate by a melt molding method. The angle of 107° was still lower than 146° of the aroid leaf. Therefore, sub-micrometer ordered roughness must be important to achieve super-hydrophobic surface on the polymer.

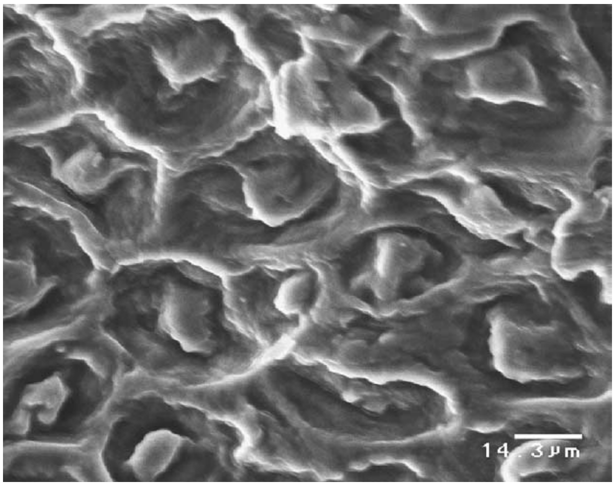

Fig. 2. Scanning electron micro photograph of the transcribed PCL surface.

Erbil et al. [12] have successfully formed a super-hydrophobic surface using polypropylene by solvent treatment. The resulting gel-like porous coating has a water contact angle of 160°. The method gives a morphology having the structure with pore size in a scale of few micrometers. This method can be also applied to a variety of surfaces as long as solvent does not dissolve the underlying material. In this study, we selected mixture solution of methanol/acetone for the chemical treatment. Both solvents and the mixture do not dissolve the PCL. Fig. 3 shows the transcribed PCL surface after soaked into methanol/acetone solution for 45 s. The treatment resulted in sub-micrometer ordered asperity pattern, although the structure is different from that of original aroid leaf. The water contact angle of the transcribed PCL with chemical treatment reached to 148°, which was higher than 146° of original aroid leaf.

Table 2 shows 10-points mean roughness (Rz) of an aroid leaf, transcribed PCL, and chemically treated PCL after transcribing. The roughness for depth direction (Rz) was estimated from SEM photographs of the cross-section of the sample. The Rz of chemically treated PCL after transcribing was almost same as that of an aroid leaf. The concavity and asperity pattern for lateral direction was also analyzed. Table 3 shows average diameter of concavity pattern (Ld), and period of sub-micrometer asperity pattern (Lp) for an aroid leaf, transcribed PCL, and chemically treated PCL after transcribing. Ld was measured directory from SEM photograph and Lp was measured from profile of brightness on SEM image. Aroid leaf surface has apparently two scaled periods. One is Ld of c.26 μm, which corresponds to the diameter of concavity pattern. Another is Lp of c.0.8 μm, corresponding to the sub-micrometer ordered asperity pattern. The transcribed PCL has only lager scaled (28 μm) period. On the other hand, two scale periods can be made on the chemical treated PCL after transcribing. The results suggested that a dualistic structure (several dozen-micrometer and sub-micrometer ordered patterns) is important for the preparation of super-hydrophobic surface on biodegradable polymers.

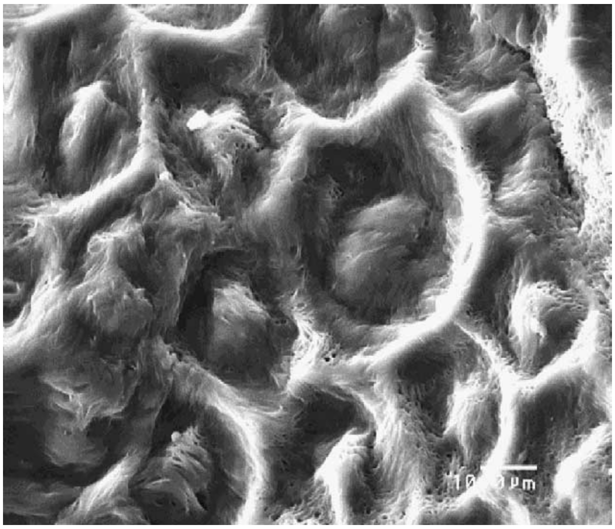

Fig. 3. Scanning electron micro photograph of the transcribed PCL surface after soaking into methanol/acetone solution.

Table 2
Ten points mean roughness (Rz) of an aroid leaf, transcribed PCL, and chemically treated PCL after transcribing

Sample	Rz (μm)
An aroid leaf	21.7
Transcribed PCL	19.8
Chemically treated PCL after transcribing	25.3

Table 3
Average diameter of concavity pattern (Ld), and period of sub-micrometer asperity pattern (Lp) for an aroid leaf, transcribed PCL, and chemically treated PCL after transcribing

Sample	Ld (μm)	Lp (μm)
An aroid leaf	26.3	0.76
Transcribed PCL	28.1	–
Chemically treated PCL after transcribing	27.4	0.85

The water-repellent natural leaves usually have antibacterial property due to the prevention of water [14,15]. In the prior studies [16,17], it is reported that *Asperugillus fumigutus* had strong degradation ability for PCL and the degradation was initiated by adsorption of the filamentous fungus on PCL surface. To investigate the antibacterial property, the transcribed PCL samples were soaked into fungus culture having isolated *A. fumigutus*. The filamentous fungus did not grow on the transcribed PCL with solvent treatment, however, it grew on the transcribed PCL without solvent treatment.

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