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Mass-producible replication of highly hydrophobic surfaces from plant leaves

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Abstract

Many plant leaves found in nature are known to exhibit a characteristic of superhydrophobicity ('lotus leaf effect'). The present study proposes a mass-production method of highly hydrophobic surfaces by simply replicating the highly hydrophobic plant leaf surfaces in two steps: the first step of making a nickel mould via electroforming and the second step of replication via a UV-nanoimprint lithography. Making a nickel mould, either a plant leaf or its negative polymer replica is used as a mandrel in electroforming, and final products become positive or negative polymer replicas of a plant leaf, respectively. It is found that the nickel-mould making using the plant leaf as a mandrel is quite successful and the final products in the form of a positive replica are better than those in the form of a negative replica in terms of replication quality and hydrophobicity. Contact angle values of the positive replicas are less than those of the natural leaves' surfaces by only 2°–5°.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over the past few years, the marvellous surface structures of superhydrophobic plant leaves, characterized by the so-called 'lotus effect', have attracted many researchers' attention [1–3]. In particular, the superhydrophobic property induced by these structures has become quite an important issue since there are a variety of practical applications utilizing their self-cleaning, drag reduction, anti-fogging effects and so on. In this regard, various methods have been reported to produce artificial hydrophobic surfaces: for instance, gel-like porous surfaces using polypropylene [4], fibrous surfaces [5–10], plasma treated surfaces [11–15], surfaces replicated from templates [16, 17], rough block copolymer surfaces [18, 19] and so on [20–34]. Besides, theoretical studies to elucidate the secrets of the water-repellent plant leaves' surfaces have also been reported [35–50].

In our recent work [51], a fabrication method has been proposed to produce highly hydrophobic films by directly

replicating the plant leaves' surfaces by means of a UV-nanoimprint lithography (UV-NIL) process, plant leaves being used as a master. Films thus produced were negative replicas of the intricate micro/nano combined structures in the original plant leaves. The hydrophobic property of the natural leaves was successfully reproduced: as a typical example, the contact angle (CA) of the replicated film of bamboo (*Phyllostachys pubescence*) leaf was measured as 145°, which is remarkably high when compared with the CA value of 152° of the leaf itself [51]. From the viewpoint of replication itself, this method can be regarded as quite a success. Unfortunately, however, this method is not appropriate for mass-production since the plant leaves can be used only once in the UV-NIL process.

For a mass-production, it is necessary to have a mould on which the same surface structures as the leaf are patterned. The mould with the patterned surface could be repeatedly used to produce polymer replicas when employed as a master in the subsequent fabrication step of the UV-NIL process. In this regard, the present study proposes a mass-production method of highly hydrophobic films by simply replicating the plant leaf surfaces in *two steps*: the first step of making a nickel mould

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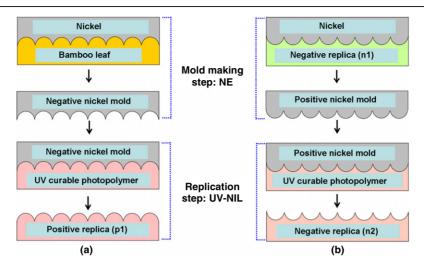


Figure 1. A schematic outline of the replication process of (a) method 1 (M1) and (b) method 2 (M2). Both replication processes are composed of two steps: the first step of mould making via nickel electroforming and the second step of replication via UV-nanoimprint lithography. In M1 the real bamboo leaf itself was directly used as a mandrel to make a negative nickel mould and subsequently the positive replica (p1) was fabricated using the negative nickel mould via UV-NIL, and in M2 the negative replica (n1) [51] of the bamboo leaf fabricated by the direct imprinting via UV-NIL was used as a mandrel to make a positive nickel mould and subsequently the negative replica (n2) was fabricated using the positive nickel mould via UV-NIL.

via electroforming and the second step of replication via UV-NIL (or via injection moulding and hot embossing processes). As far as the first step of nickel-mould making is concerned, one could use a plant leaf itself, if possible, as a mandrel in electroforming or could make use of its negative polymer replica (produced from the aforementioned method [51]) as a mandrel. The latter is a relatively well established method, whereas the former has never been attempted to the best of our knowledge. In this study, both the two approaches have been carried out with four kinds of plant leaves. In the following sections, bamboo is taken as a typical example to describe the experimental procedure and to discuss basic results, followed by a brief report associated with the three other leaves.

2. Proposed fabrication methods

The proposed method consists of two steps: the first is a mould making step via nickel electroforming (NE) and the second step is the UV-NIL process to produce polymer replicas using the mould. As mentioned above, either a plant leaf itself or its negative polymer replica can be used as a mandrel in NE. For the sake of clear presentation, the overall method with the former and the latter case are hereinafter called method 1 (M1) and method 2 (M2), respectively. Figure 1 schematically represents both M1 and M2. They differ from each other in the mould making step when M1 and M2 use the leaf itself and its negative polymer replica, respectively. (It may be noted that the negative polymer replica can be made via the UV-NIL process using the leaf as a master, as described in detail in [51].) As indicated in figure 1, the final products become positive and negative replicas of the original plant leaf surface for M1 and M2, respectively. It may be mentioned that this fabrication method does not need a clean room environment.

More detailed procedures are described in the following sections.

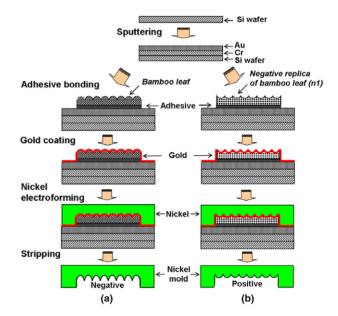


Figure 2. Schematics of nickel-mould making process in M1 and M2. (a) Negative nickel mould for M1 patterned upon the bamboo leaf itself; (b) positive nickel mould for M2 patterned upon the negative replica (n1) [51] of the bamboo leaf.

2.1. First step: mould making

Figure 2 schematically shows the mould making process by means of electroforming. A silicon wafer is first coated with chromium (20 nm thick) to promote adhesion of the gold layer (80 nm thick) on the silicon wafer. The gold layer is deposited on the chromium layer by an ion sputtering system (BJD 1800, TEMESCAL, USA), serving as a nickel seed layer. Next, bamboo leaf in the case of M1 (figure 2(a)) (or its negative polymer replica in the case of M2, denoted by n1 in figure 2(b)) is bonded on the substrate with the help of an adhesive

Table 1. Nickel electroforming processing conditions.

| Parameter | Value |
|--|---------|
| Temperature (°C) | 55 |
| Current density (mA dm ⁻²) | 0.3–1.3 |
| pH | 4.1 |

(Loctite, PRISM 401). Since the leaf or its negative polymer replica is not electrically conductive, a gold coating (Paraone, PS-1200, Korea) is performed on the leaf or its negative replica surface including the previous gold layer. NE is then carried out under the processing conditions given in table 1. Finally, unnecessary layers (silicon, chromium, gold and bamboo leaf or negative polymer replica) are stripped, resulting in a pure nickel mould.

As far as the stripping is concerned, firstly to remove the silicon layer, the nickel mould is dipped into 70 °C potassium hydroxide (KOH) solution. Secondly, in order to remove the chromium layer, the mould is dipped into CR-7SK solution (Cyantek Corporation, USA) at room temperature. Then the gold layer is removed in a stripper solution (mixture of 40 g of potassium iodide, 10 g iodine and 400 ml water) at room temperature. Finally, the bamboo leaf (or polymer replica) is peeled off when the mould is dipped into the 70 °C KOH solution.

2.2. Second step: film fabrication via UV-NIL

Figure 3 schematically shows UV-NIL equipment and the fabrication process of polymer replicas using a nickel mould (obtained from the mould making step) via the UV-NIL process. The UV-NIL equipment was designed and manufactured by our research group [51].

The UV-NIL process is carried out as follows: setting up the processing conditions and the sequence on the PC which controls the whole system, fixing the nickel mould to the vacuum chuck, dispensing UV curable photopolymer on a slide glass, removing air and dust from the vacuum chamber, applying a regulated force to the vacuum chuck system (where the mould is fixed) via a pneumatic cylinder (SMC Korea, model MB8F40-KRG0474-175-NH), exposing the photopolymer to collimated UV light through the quartz plate using a UV lamp and a lamp shutter, and, finally, detaching the polymer replica from the nickel mould. The UV curable photopolymer used in this work is RenShape SL 5180 (Vantico Inc., density $1.15\times10^3~kg~m^{-3}$, viscosity 0.24 kg m⁻¹ s⁻¹, critical exposure 13.3 mJ cm⁻²). The UV lamp adopted in this system is MRL 1500 (SEN Inc. Japan, lamp wavelength 365 nm, lamp effective area $125 \times 125 \text{ mm}^2$, lamp power 1.5 kW).

3. Characterization of the replicas

The replication quality and surface property of the polymer replicas are characterized by scanning electron microscope (SEM) and water contact angle (CA). Scanning electron micrographs of the nickel moulds and their corresponding polymer replicas are taken by an XL 30S (FEI, USA) scanning electron microscope (SEM). Water CA is measured by a sessile drop method using a Krüss drop shape analysis system (Krüss

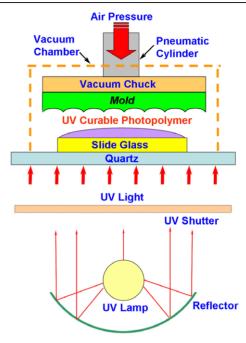


Figure 3. Schematic diagrams of the UV-NIL process using a nickel mould. In the case of **M1**, using the negative nickel mould directly patterned upon the bamboo leaf, the UV-NIL process produces positive replicas (**p1**, in figure 1(a)). In the case of **M2**, using the positive nickel mould patterned upon the negative replica (**n1**) [51], this process provides negative replicas (**n2**, in figure 1(b)).

GmbH Germany, model DSA 10-Mk2) with the distilled water droplet volume of 5 μ l. This system automatically puts a water droplet on the surface by firstly pushing down the droplet and then releasing it on the surface, without allowing user control, and then a CCD camera captures the shape of the droplet on the surface, from which the contact angle is analysed by commercial software (SCALE 2.0, Paraguay). Contact angles were measured at least ten distinct positions and averaged for each case to be reported in this work.

In order to establish a reference CA value for comparing with the produced replicas, a flat and smooth UV photopolymer (RenShape SL 5180) surface is prepared using a self-assembled monolayer (SAM) laid flat on a silicon wafer as a master (instead of the mould in figure 3) in the UV-NIL equipment. The monolayer is deposited on the silicon wafer surface through the vapour evaporation method [52] using 1H,1H,2H,2H-perfluorodecyltrichlorosilane ($C_{10}H_4C_{13}F_{17}Si$) as an anti-adhesion layer to provide a low surface energy coating for better mould release after imprinting. The reference CA is found to be about 56°.

4. Results and discussion

As previously stated, one could use a plant leaf itself (in M1) or its negative polymer replica (in M2) as a mandrel in nickel-mould making, and the final products become positive and negative replicas of the original plant leaf surface for M1 and M2, respectively. If one believes that the evolution of nature provides an optimum form of plant leaf surface topography, the positive replicas are in accordance with nature. It is expected that positive replicas may have a superior hydrophobicity to

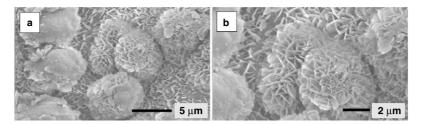


Figure 4. SEM images of a real bamboo leaf surface in two magnification factors.

negative replicas since the former are closer to the naturegiven topography. In this sense, M1 would be more desirable than M2.

Nickel electroforming over a polymer structure is well established and thus has been frequently introduced by many researchers [53]. On the other hand, making a mould out of a natural leaf has never been reported in the literature to the best of our knowledge. In this regard, M2 is easier than M1 with respect to nickel-mould making. At the initiation point of this work, it remained to be found how accurately one could copy the intricate surface structures of a leaf on the nickel-mould surface via NE. In this regard, M2 was executed first, followed by M1.

4.1. Replication quality of the surface patterns

There are many processing parameters affecting the final quality of replicas: (i) important parameters associated with the UV-NIL process are UV light strength, UV light exposure time and applied pressure on the photopolymer resin; (ii) parameters associated with NE is the electric current density. In particular, the appropriate UV light exposure time varies with the volume of the photopolymer to be cured sufficiently before detaching the replica from the mould. It was found that the appropriate air pressure in the pneumatic cylinder was about 400 kPa in this work. Furthermore, it may be noted that, for fine replication of intricate micro/nano combined structures onto a nickel mould, one needs to start with a low value of electric current density at the initial stage of NE and then to increase the value gradually to a constant one at the end.

According to the proposed method, two nickel moulds were fabricated and subsequently their corresponding replicas were produced. In the following discussion, the final product in the form of a positive replica from M1 is referred to as p1 and the negative polymer replica to be used in mould making in M2 [51] is denoted by n1, while the final product of M2 in the form of a negative replica is denoted by n2.

Figure 4 shows SEM images of the real bamboo leaf surface which has multi-scaled structures, that is, a combination of micro- and nano-structures. Rose quartz petallike nanostructures exist on protruding micro-patterns of about 5 μ m in size. SEM images of surfaces obtained from each step of M2 are first presented in figure 5: (a) the negative polymer replica (n1), (b) the positive nickel mould obtained from the mould making step using n1 in figure 1(b) and (c), the final product n2, respectively. Figure 5(a) shows that nanostructures are not so well replicated as the microstructures in n1 [51]. Consequently, the nanoscale structures are poorly replicated in the mould (figure 5(b)) even if the microscale structures are

well reproduced when compared with figures 4 and 5(a). The nanoscaled indentations on the mould surface in figure 5(b), which looks different from the topography of n1 in figure 5(a), could be attributed to the poor deposition of nickel in the beginning stage of NE. Since the leaf has protruding patterns, the final product in the form of negative replica (n2) naturally has indented surface structures (figure 5(c)).

Notwithstanding the initial concern in this work, a nickel mould was successfully obtained from the nickel electroforming process in M1 as shown in figure 6(a). In the M1 case, the electric current density is increased gradually from a lower value than the M2 case to the same constant value in NE, resulting in finer deposition of nickel onto nanoscaled structures at the beginning stage of NE. As compared with figure 4, figure 6(a) indicates that the mould successfully replicates not only the microstructures of the leaf but also its fine nanostructures. The final product (p1) shown in figure 6(b) is a good negative replication of the mould (figure 6(a)), which in turn is a positive replica of the original leaf (figure 4) at a satisfactory level with respect to the similarity from the microto the nanoscale structures. The better replication quality of M1 than M2 seems to be attributed mainly to the fewer steps involved in M1.

4.2. Contact angle as a measure of hydrophobicity

To evaluate the practicability of the proposed replication method for mass-production using natural leaves, CA is a good indicator in the sense that the obtained film would be useful due to its water repellency and water CA is a well accepted measure of hydrophobicity. Measured CA values are compared for three kinds of polymer replicas: n1 (figure 5(a)), n2 (figure 5(c)), p1 (figure 6(b)). Figure 7 shows water drops on various surfaces: (a) a real bamboo leaf, (b) a negative replica **n1**, (c) a negative replica **n2**, (d) a positive replica **p1**, and (e) a flat and smooth polymer film. The CA value of the real bamboo surface is 152°, indicating high hydrophobicity. The CA values for the three polymer replicas are 145° for n1, 141° for n2, and 150° for p1. p1, the final product of M1 has the highest CA among the three replicas as expected, just a little smaller than the bamboo leaf itself (figure 7(a)), only by 2° . On the other hand, n2, the final product of M2, has the lowest CA due to three replication steps involved in M2, in particular, due to the poor replication of nanoscale features of leaf surface onto the nickel mould of M2 as mentioned before. As expected, M1 results in a better replica of the highly hydrophobic leaf surface than M2. It may be noted that the CA value was also measured on a flat and smooth surface of the same polymer (with no micro/nanostructures) for a reference value, which turns out to be 56°.

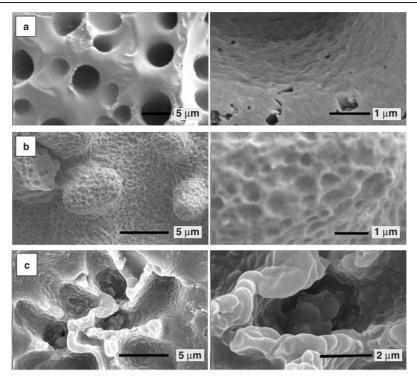


Figure 5. SEM images associated with M2: (a) negative polymer replica, n1, of bamboo leaf obtained via UV-NIL [51]; (b) positive nickel-mould surface patterned upon the negative replica (n1) for M2 and (c) the final product of M2 in the form of a negative replica (n2) from the positive nickel mould (b). In each row, the right images are the magnified images of the left ones.

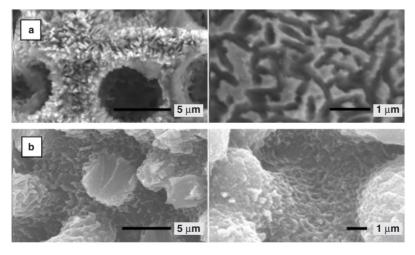


Figure 6. SEM images associated with **M1**: (a) negative nickel mould patterned upon the bamboo leaf surface (figure 4) and (b) the final product in the form of a positive replica, **p1**, from the negative nickel mould (a). In each row, the right images are the magnified images of the left ones.

The smooth polymer film used in this study is hydrophilic. According to the experimental results so far, all the replicas become hydrophobic, their CAs being much higher than the reference flat film even if the films are made of the same material as the flat film. This consistent observation of changing the hydrophilicity to hydrophobicity could be explained by the change of their topographical features, namely the micro/nano combined structures of polymer replicas. There are many research reports on hydrophobicity induced by surface roughness [35–50]. In most reports, surface

roughness enhances the hydrophobicity when materials are hydrophobic [21]. On the other hand, our previous work [51] has reported that hydrophobicity could be achieved from hydrophilic material by surface roughness, which corresponds to the observation of **n1** in this work. At this point, it might be recalled that hydrophobicity can be also achieved from hydrophilic material by surface coating or chemical treatments [12, 34]. Hence, one could conjecture that the hydrophobicity in **n1** might be due to some wax material of the plant leaf surface being transferred and remaining on

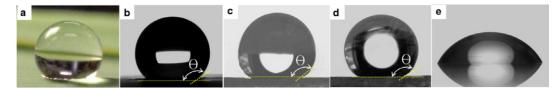


Figure 7. 5 μ l water drops on the various surfaces. (a) Original bamboo leaf (figure 4), (b) negative polymer replica (n1) [51] of the bamboo leaf (figure 5(a)), (c) negative replica (n2) by M2 (figure 5(c)), (d) positive replica (p1) by M1 (figure 6(b)), and (e) flat and smooth surface. The contact angles (average \pm standard deviation) of these surfaces were (a) $152^{\circ} \pm 2.9^{\circ}$; (b) $145^{\circ} \pm 3.4^{\circ}$; (c) $141^{\circ} \pm 2.1^{\circ}$; (d) $150^{\circ} \pm 2.5^{\circ}$; (e) $56^{\circ} \pm 1.2^{\circ}$.

the polymer replicas after UV-NIL, of which the possibility could not be completely ruled out. The present study certainly clarifies this unresolved issue of the doubtful effect of wax, in addition to the effect of micro/nano combined structure, on the increase of CA value as follows. According to the results obtained in this work, the contribution of the chemical property of wax to the increase of hydrophobicity in n2 from M2 and p1 from M1 could now be surely ruled out since there is no possibility for wax existing on the pure nickel moulds and on subsequent polymer replicas obtained from the mould. Therefore, it is now safe to claim that micro/nano combined structures can transform even the hydrophilic flat surface to a highly hydrophobic rough surface.

According to the Cassie-Baxter theory [49], the hydrophobicity increases with the ratio of the air surface to the solid surface. Air entrapped in the rough surface could enhance its water-repellency since the water drop can sit partially on air, not on the entire solid surface. Based on this theory, many researchers have introduced surface roughness by patterning either microstructures [35] or nanostructures [15] via various lithography technologies to achieve hydrophobicity to some extent. In comparison with just patterned microstructures or nanostructures, the intricate nanostructures spread over microstructures in the plant leaves from nature seem to be capable of keeping more air entrapment, resulting in superhydrophobicity [40]. In the same manner, the micro/nano combined structures on n1, n2 and p1 can also have more air entrapment, giving rise to high hydrophobicity of the polymer replicas, regardless of the hydrophilicity or hydrophobicity of the material itself.

Up to this point, the successful replication of the intricate micro/nano combined structures of the bamboo leaf has been demonstrated as a typical example. One may want to make sure that the same method can be successfully applied to various plant leaves. In this regard, three other plant leaves (tulip tree (Liriodendron tulipifeva L.), silver maple tree (Acer saccharinum L.), and lovegrass (Eragrostis terruginea)) were selected to validate the general applicability of the proposed method for mass-production. To no surprise, negative nickel moulds and subsequently positive replicas were successfully fabricated from the procedure of M1. Figure 8 shows SEM images of plant leaves, their negative nickel moulds and corresponding positive polymer replicas from M1 for three plant leaves. As indicated in figure 8, the replicas are quite similar to the original leaf surfaces in terms of their micro/nano combined structures. The measured CA values in these cases are listed in table 2. CA values of all the replicas are less than those of the natural surfaces only by 3°-5°, indicating their high hydrophobicity to our satisfaction.

Table 2. Contact angle values of plant leaves and their corresponding positive polymer replicas from M1.

| (Average \pm standard deviation) | | | |
|------------------------------------|--|----------------------------|--|
| | Tulip tree | Silver maple tree | Lovegrass |
| Leaf Positive replica | $148^{\circ} \pm 1.7^{\circ}$ $143^{\circ} \pm 2.3^{\circ}$ | 149° ± 2.3° 145° ± 3.4° | $154^{\circ} \pm 3.7^{\circ}$ $151^{\circ} \pm 2.2^{\circ}$ |

5. Concluding remarks

The present study proposes a successful mass-production method of highly hydrophobic polymer films by simply replicating the plant leaf surfaces in two steps: the first step of making a nickel mould via electroforming and the second step of replication via UV-NIL. As far as the nickel-mould making step is concerned, two kinds of mandrels in electroforming process could be introduced, either a plant leaf or its negative polymer replica, and final products become positive or negative polymer replicas. The methods in the former and latter cases are referred to as M1 and M2, respectively. The final products from M1 are better than M2 with respect to both the replication quality and the hydrophobicity. It may be noteworthy that the success of M1 is attributed to the successful electroforming directly over plant leaves, which has never been attempted in the literature to our best knowledge. We regard the detailed procedure (described in section 2.1) of electroforming over the natural leaf surface employed in this work as a new mould making technique for a mould insert to be used in replicating positive replicas from nature directly.

Measured CA values of final products from the bamboo leaf are 141° for the negative polymer replica from M2 and 150° for the positive polymer replica from M1, to be compared with the CA value of 152° for the real bamboo leaf. The positive replica from M1 is found to be better, as expected, since it has the topographical features close to the natural leaf surface. This level of hydrophobicity is attributed to the surface topographic features, namely micro/nano combined structures, regardless of the hydrophilicity or hydrophobicity of material itself.

Furthermore, M1 has also been found to be successfully applied to many highly hydrophobic plant leaves from nature. In this regard, M1 could be recommended as one of the suitable mass-production methods for highly hydrophobic films utilizing natural leaves. It may be further mentioned that UV-NIL for the second step can be replaced with PDMS casting, injection moulding or hot embossing processes, since the nickel mould prepared by M1 can also be utilized as a mould insert regardless of fabrication technologies. In

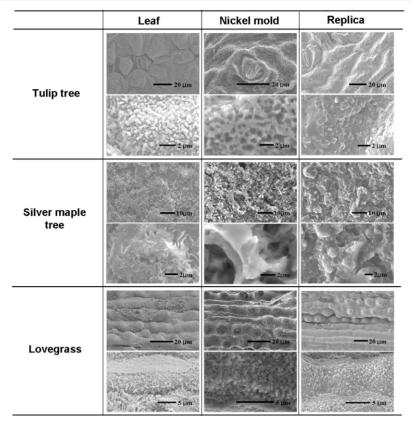


Figure 8. SEM images of the plant leaves, negative nickel moulds and positive polymer replicas of the diverse plant leaves. In each row, the lower images are the magnified images of the upper ones.

particular, injection moulding or hot embossing processes can be better in terms of cost effectiveness and mass-production capability than UV-NIL and, more importantly, enable final replica products of various polymeric materials such as polystyrene (PS), poly(methyl methacrylate) (PMMA), polycarbonate (PC), cyclic olefin copolymer (COC) and so on.

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