Stereolithography of Natural Rubber Latex, a Highly Elastic Material

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ABSTRACT

Typically, natural rubber (NR) offers a wide range of applications because of its exceptional mechanical properties, particularly elasticity. However, due to its unique mechanism of vulcanization, 3D fabrication techniques with NR is still to be explored. Vulcanization is necessary to form crosslinks between the NR chains and greatly improve its elasticity and tensile strength. In this study, the pre-vulcanized NR latex was prepared for the stereolithography (SLA) process to additively manufacture highly elastic parts. Process parameters were studied to investigate the feasibility of the fabrication. The parameters include laser power, scan speed, and layer thickness. This work demonstrates a promising 3D fabrication technique using the NR latex that achieves mechanical properties and crosslink density comparable to those from the conventional processes.

Introduction

Natural rubber (NR) is typically harvested as a milky white fluid from a rubber tree (*Hevea brasiliensis*) through a process called rubber tapping. Inheriting a superior flexibility, NR compound products offer a wide range of applications including tires, rubber seals, energy absorbers, disposable gloves, condoms, etc. Most of the products are traditionally fabricated by extrusion, calendaring, or molding. These conventional methods rely solely on molds and dies, limiting the design freedom and the possibility of product customization. During the past centuries, additive manufacturing (AM) was introduced to enable the fabrication of end-use products with unique and intricate geometries as well as tailor-made designs.

As widely perceived, AM is the key technique for mass customization and personalized products. There are extensive applications of additively manufactured elastomeric materials [1–4], for instance, insoles, soft robotics, stretchable electronics devices, etc. Combined with the unique mechanical properties of the NR, an unlimited design freedom derived from AM enables a wide variety of the product elasticity and cellular structure gradient for functional components. Hence, developing an AM technique for the NR is essentially a paradigm shift of the NR-product design and manufacturing that offer an immense drive for the economics of rubber cultivating communities. However, most of the AM technologies for polymeric materials were developed for thermoplastic, thermoset, and synthetic elastomeric polymers [5–9]. There have been no commercially available AM techniques for the NR.

Previously, the printability of elastomeric latex materials, including the NR, was studied using an ink-jet printing technique [10]. With various latex mixtures systematically compounded, this study found the synthetic mixtures with the proper viscosities best suited for the process. The NR latex was also used in the study but did not show a good printability. Recently, a drop-on-demand (DoD) technique was also developed for the NR latex [11]. The proposed process gave promising results with a tensile strength of 5.44-13.5 MPa and an elongation at break of 480%.

However, the extruded material was as wide as 1 mm, exhibiting relatively coarse details. In order to fabricate the rubber components with more delicate features, the stereolithography (SLA) technique is proposed in this paper.

In contrast to the crosslinking process for photopolymers in typical 3D printing techniques, the NR molecular structure only crosslinks through a unique process called vulcanization. Technically, it is necessary to mix the NR latex with some additives in the vulcanization processes to crosslink and improve its mechanical strength and stability. The latex is subsequently dried to become solid.

Our research group has previously developed a patent-pending technique of the AM for the NR latex [12]. Feedstock of the process is a liquid form of the NR that requires the pre-vulcanization procedure, which is a process that crosslinks the individual rubber particles in latex without destroying a colloidal character. In previous studies, pre-vulcanized latex were prepared using two methods: (1) sulfur pre-vulcanization and (2) radiation-initiated pre-vulcanization [12,13]. An experimental study revealed that the sulfur pre-vulcanized NR latex yielded a better physical appearance of the additively manufactured rubber artifact. However, the most preferred set of process parameters was still undetermined. As a result, this study focuses on the parametric study of the 3D fabrication of the sulfur pre-vulcanized NR latex. Typically, there is a strong relationship between the laser energy density and the quality of the samples. The laser power, layer thickness, and scan speed were varied to reflect different levels of the laser energy density. The quality of the rubber samples was characterized by the morphology of the surface under a microscope. The best known combination of the process parameters was subsequently used to produce specimens for certain mechanical tests and equilibrium swelling tests from which the results were compared to those of conventionally fabricated specimens. In addition, a rubber sample with fine features was fabricated to demonstrate the potential of the fabrication technique proposed in this work.

Methodology

The parametric study was conducted using an in-house developed SLA machine shown in Figure 1 and Figure 2. The machine is equipped with a pulsed laser of 355-nm wavelength with the maximum power of 4 W. To study the effect of the laser energy density, the laser power, layer thickness, and scan speed were considered to be the key process parameters that affect the level of the laser energy density. These parameters were included in the experiment design for a comprehensive study of the process. The experiments for the parametric study were outlined in Table 1.

The frequency of the pulsed laser was fixed at 20 kHz. The scanning pattern was a unidirectional crosshatch with 100-μm hatch space and orientation of 0 and 90 degrees in each pass. The feedstock of the process was prepared using concentrated NR latex produced by a centrifugation process of ammonia-preserved NR latex. The latex was mixed with an accelerator, an initiator, a coagent, an antidegradant, and an activator that are subsequently pre-vulcanized with the sulfur addition. Then, a heat-sensitive processing aid was subsequently blended into the pre-vulcanized latex compound at the temperature of 20 °C for one hour. The pre-vulcanized latex was further diluted to obtain the level of total solid content of 50%. A vat of the NR latex was prepared for the laser irradiation. Each layer of the latex was formed by a recoater blade at a determined

layer thickness that is controlled by a vertical displacement of the platform. The surface of the latex is selectively irradiated by a laser beam to form a semi-solid layer.
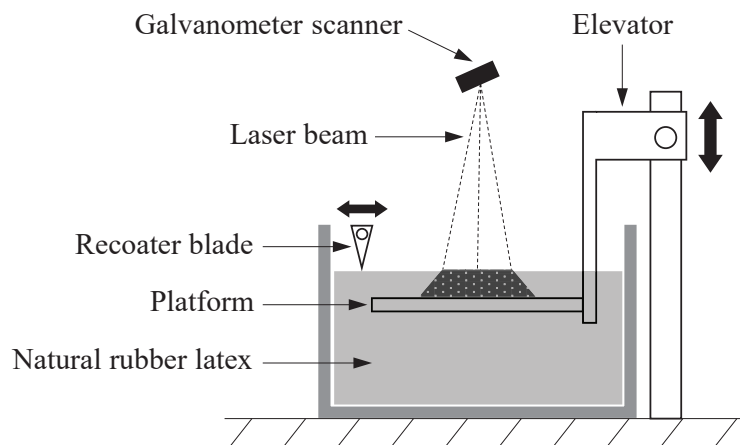
Figure 1 Diagram of the in-house developed SLA machine

(a)   (b)
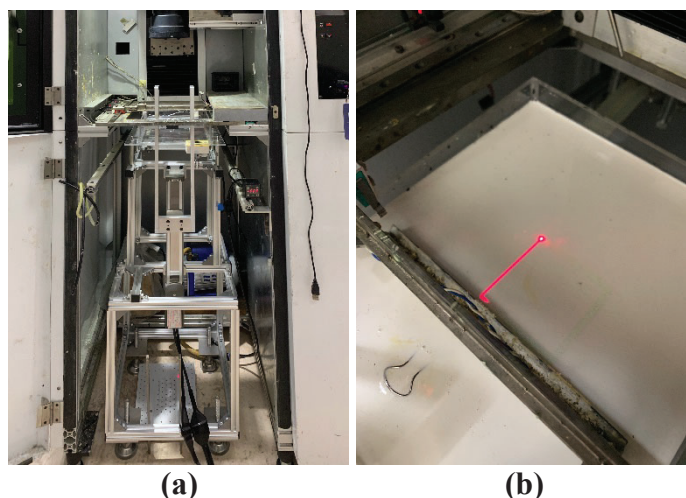
Figure 2 (a) Setup of the in-house developed SLA machine and (b) surface of the NR latex

Table 1 Process parameters and levels

Parameters	Levels
Layer thickness (μm)	200, 300
Laser power (%)	60, 80, 100
Scan speed (mm/s)	40, 50, 60

A single layer of 10 mm by 10 mm squares was fabricated at different combinations of process parameters. An optical microscope was used to inspect the sample morphology. The best-known combination of the process parameters was subsequently determined, and three specimens were additively manufactured for mechanical test and equilibrium swelling test. The mechanical test was conducted under the ASTM D412 standard with the rate of grip separation of 500±50 mm/min. The equilibrium swelling test was conducted using toluene and crosslink densities of the samples were calculated by using the Flory-Rehner equation. In both tests, the specimens were

required to be 0.3-1.0 mm thick, which comprises three layers of the additively manufactured NR. Another set of specimens was fabricated by a conventional air-dry process for comparison. Using the same NR latex compound, a glass mold with the required thickness was filled with the latex and stored at a room temperature until the specimens were completely solidified.

Results and Discussion

Figure 3 and Figure 4 illustrate the surface morphology of each sample observed under an optical microscope, with 200-μm and 300- μm thickness, respectively. The figures clearly assure that the appearance of the surface can possibly be used as an index to assess the quality of the samples. As the NR is naturally an unsaturated polymer, the material is highly vulnerable to an excess heat due to its thermal degradation mechanism. As a result, the samples became somewhat tacky when the laser energy density was too high. The degradation of the rubber can be observed by the shiny surfaces and also the physical condition of a tacky surface shown through the micrographs. On the other hand, when the laser energy density is scarce, sufficient heat is not transferred into the layer of the NR latex. If this is the case, the 3D part cannot be formed, since the solidified line after the laser exposure is rather flimsy to connect to the neighboring line.
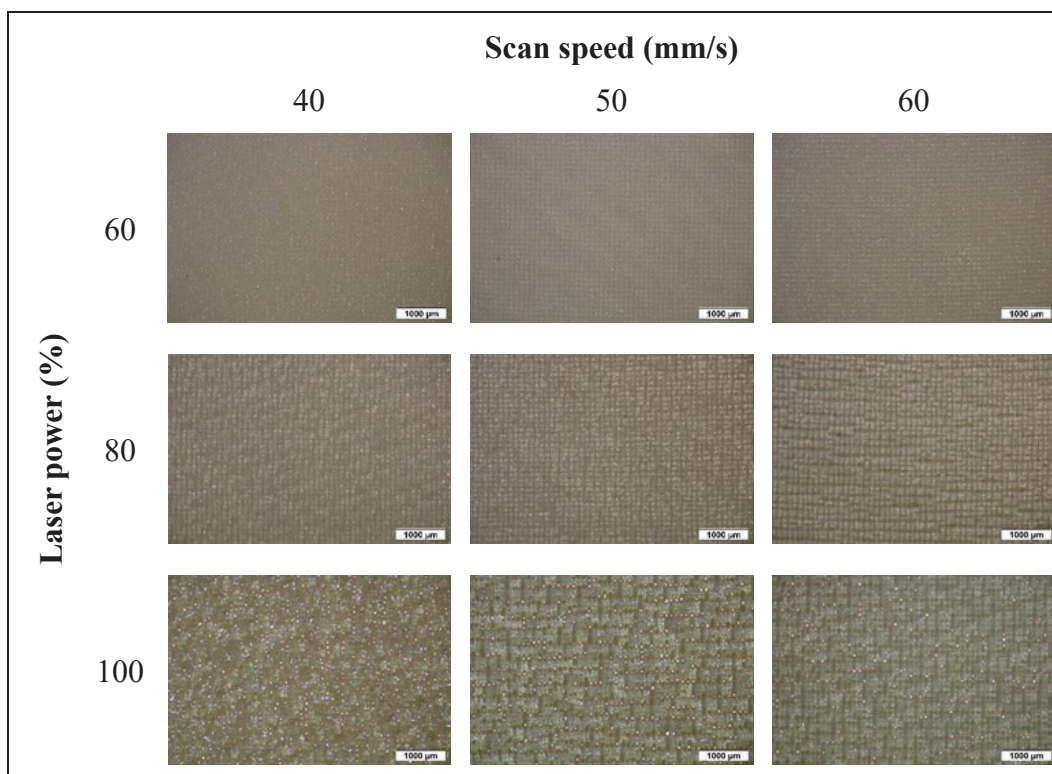
Figure 3 Surface morphology of the samples with the layer thickness of 200 μm
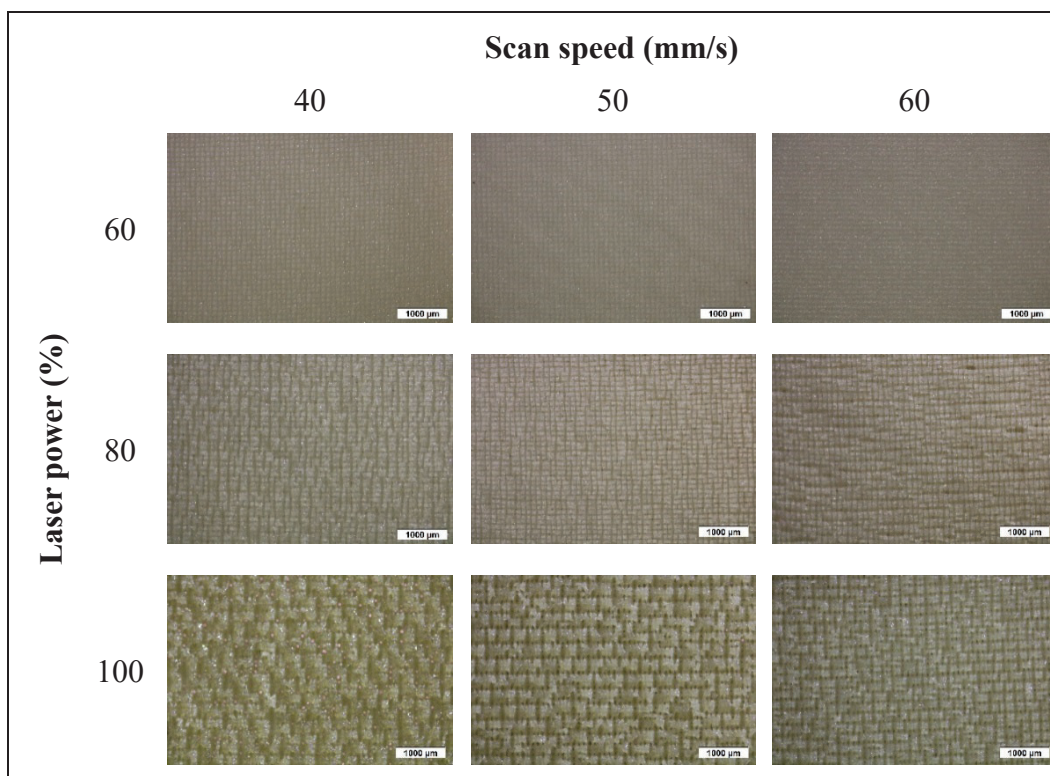
Figure 4 Surface morphology of the samples with the layer thickness of 300 μm

Furthermore, the results illustrate that the laser power and the scan speed significantly affect the surface morphology. However, the samples with the layer thickness of 200 μm and 300 μm show similar visual appearance when the other two parameters were fixed at the same levels. Basically, using a thinner layer thickness was a better alternative, since the part features, e.g. slopes on a vertical wall, can be fabricated at a finer resolution and a higher accuracy. As a result, the layer thickness is preferably 200 μm. Considering the effect of the scan speed, a lower scan speed results in the degradation of rubber due to an excessively high laser power density, especially when the laser power is also high. Besides that, the laser power affects the quality of the samples in the similar fashion; namely, an intense laser exposure leads to degradation of the rubber. Based on the surface observation, it can be concluded that the best found set of process parameters in this study is the layer thickness of 200 μm, the laser power of 80%, and the scan speed of 50 mm/s. These parameters were later used to fabricate the specimens for the mechanical tests.

Table 2 shows that the tensile strength and the hardness of the additively manufactured specimens are slightly lower than those of the conventionally fabricated ones, while the elongation at break is slightly higher than that of the conventionally fabricated specimens. It can be concluded that the additively manufactured NR is slightly softer and more flexible than the NR from the conventional process. The mechanical properties agrees with the results from the equilibrium swelling test. The crosslink densities of the additively manufactured samples were 0.100 ± 0.003 mmol/cm³ which is slightly lower than that of the conventionally fabricated samples 0.130 ± 0.003 mmol/cm³. However, because of the insignificant discrepancy of the results, it is still indefinite to conclude that this technique of 3D fabrication using the NR latex yields the mechanical properties identical to those from the conventional processes.

Table 2 Mechanical properties of the rubber specimens

Test specimens	Hardness (Shore A)	Modulus at 100% elongation (MPa)	Modulus at 300% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)
Additively manufactured samples	31.7	0.69±0.06	1.27±0.07	17.1±3.69	757±21
Conventionally fabricated samples	41.7	0.90±0.04	1.62±0.05	19.99±1.73	705±1

Subsequently, NR samples with a cellular structure were fabricated using the in-house developed SLA machine to demonstrate the potential of the technology with the best known set of process parameters. Seven layers of the latex were formed into a 3D part shown in Figure 5. The fabricated sample with the cellular features reveals that the latex mixture and SLA process developed in this work is capable of producing a customized components with tailored cellular sizes and stiffness gradient.

| (a) | (b) |
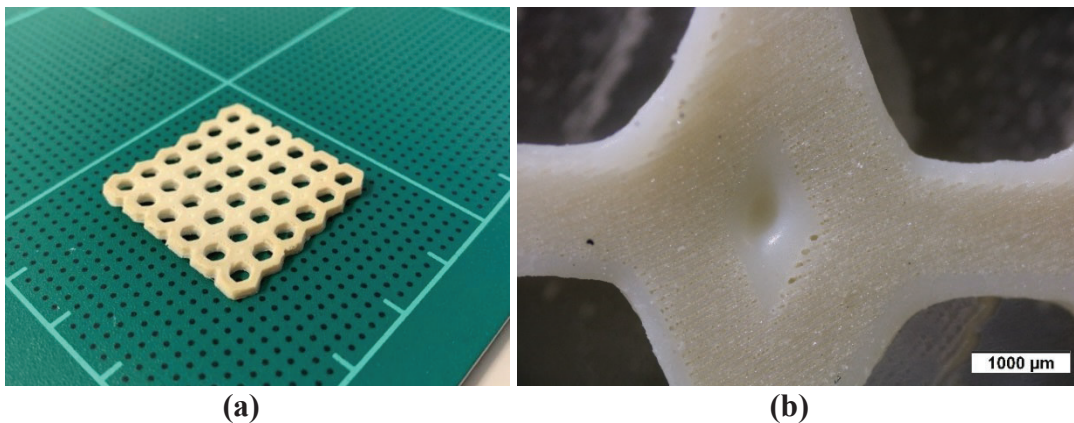
Figure 5 (a) Additively manufactured rubber artifact with cellular structure and (b) its micrograph

Conclusions

The pre-vulcanized NR latex was used to 3D fabricate highly elastic samples by the in-house developed SLA machine. The process parameters were studied to investigate the effects of the laser power density on the fabrication process, particularly the surface morphology. The parameters include the laser power, the scan speed, and the layer thickness. The best known set of process parameters in this study is the laser power of 80% (approximately 3.2 W), the scan speed of 50 mm/s, and the layer thickness of 200 μm. The mechanical tests were conducted to compare the properties of the additively manufactured and the conventionally fabricated samples. The results revealed that the tensile strength, the elongation at break, the hardness, and the crosslink density of the specimens manufactured from both processes are relatively comparable. Besides that, it can be concluded that this novel technique for AM of the NR is capable of fabricating rubber

parts that are comparatively strong and flexible when compared to those from conventional processes.

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