ABSTRACT: Natural rubber (NR), a natural product from the Hevea brasiliensis tree, has been developed as a photosensitive mechanical modifier utilized in lithography-based three-dimensional (3D) printing technology. Here, we transformed NR to photosensitive NR (PNR) by incorporating acrylate groups via chemical modifications. The acrylated NR was blended with a commercial resin (CR) at various rubber contents (0 to 3 wt %) by a simple mixing approach. The blended resin was solidified to pattern the desired specimen using a digital light processing-based 3D printer. The effect of PNR contents on mechanical properties and thermal performance of the printed specimen compared to the neat CR was studied in this work. A printed sample containing 1.5 wt % PNR can increase the elongation ability and impact strength by approximately 59 and 116%, respectively, compared to the neat CR. The microstructure of the printed objects shows a heterogeneous surface consisting of dispersed rubber droplets and a continuous CR matrix. Two glass transition temperatures belonging to the rubber phase and the resin matrix can be observed. The thermal decomposition of the printed part decreased slightly with the elevation in the rubber content. Consequently, the synthesized photosensitive natural rubber could be used as a toughness modifier employed in ultraviolet-curable resin for the light-based 3D printing technology.

1. INTRODUCTION

Three-dimensional (3D) printing, a solid free-form fabrication or rapid prototyping technology, is an emerging challenge with various application fields. This technology can utilize various materials and create many 3D objects, leading to an exciting technology.1,2 Generally, 3D printing is an additive manufacturing (AM) process that refers to introduction of a thin layer in a micrometer scale to construct a 3D physical object directly through a digital model with a layer-by-layer deposition process.3–5 The well-known features of the 3D printing process over the traditional manufacturing process include complex geometries, freedom in customization, less waste, and tool-less production.6–8 Recently, the global 3D printing market attracts growing interest and creates an impact on the commercial and industrial sectors with limitless and continuous breakthroughs, expanding the economy of 3D printing technology.9 Several 3D printing techniques are utilized for efficient fabrication of complex-shape products. Digital light processing (DLP)-type 3D printing is one of the typical AM processes and is extensively recognized with several notable aspects, including high printing accuracy, sophisticated design, high speed, low volatile organic solvents, and low energy consumption. Furthermore, it allows high resolution in the XY direction and the Z-axis.10,11 The DLP technique involves a spatially controlled solidification of liquid photosensitive resin via photopolymerization reaction to complete the required part using the projection of ultraviolet (UV) exposure, creating cross-linking or interpenetrating polymer networks.12,13

Over the past decades, many attempts have paid attention to photosensitive materials from alternative resources to solve significant issues caused by environmental pollution and the scarcity of petroleum reservoirs.14–20 A tremendously growing interest in photocurable polymers derived from natural feedstock for lithographic 3D printing technology has been continuously reported. Voet et al. demonstrated the successful fabrication of printed objects by a biobased acrylate photocurable resin using a commercial stereolithography technique.3 Natural phenolic-based (meth)acrylates were prepared for utilization in a lithography-based 3D printer by Ding and co-workers.17 They revealed a sustainable and...
versatile material of natural phenolic acrylates with high-performance 3D printing. Soybean oil-based methacrylate resin for utilization in commercial lithographic 3D printers was synthesized by Guit and co-workers. The result demonstrated accurate printing quality with complete layer fusion. Rigidity and toughness could be adjusted by varying the composition and the number of methacrylate functional groups. Vanillin is a naturally occurring molecule derived from lignin. Bassett et al. prepared vanillin-based vinyl ester resin for AM applications. They demonstrated that the resin containing vanillin-based vinyl ester can potentially tune the cure characteristics and printed polymer properties. Functionalized sucrose ester resin was explored for lithographic printing by Silbert and groups. They demonstrated that this synthesized material can be incorporated into a 3D printing resin formulation, and it can be printed in different orientations.

Natural rubber (NR), a green elastomeric and renewable polymer with mass feedstock in Thailand, can be derived from the Hevea brasiliense tree. It is composed mainly of cis-1,4 isoprene moieties. With various notable aspects, including high strength, excellent flexibility, easy chemical modification, and biodegradability, NR has attracted enormous attention in various applications. Several researchers have reported the development of photosensitive materials derived from NR to employ in adhesive and coating applications. Phinyocheep and Duangthong synthesized acrylated epoxidized liquid natural rubber as a photosensitive elastomeric material and succeeded in studying the photocross-linking reaction by the photo-calorimetric method. Kwanming et al. prepared a liquid NR-based acrylate material and designed a resin formulation for the UV curing process in surface coating application. Zhang et al. presented a new pathway to replace the traditional vulcanization process in rubber production. They prepared an NR-based photosensitive polymer cross-linked with star-shaped polystyrene for elastic sealing materials utilizing a particular complex-shape part. Fumarized alkyd incorporated with epoxidized NR (ENR) was synthesized for coating application by Ang et al. They revealed improvement of film properties with the introduction of ENR into the coating formulations. Based on our knowledge, up to now, utilization of NR as a photosensitive elastomeric material in the light-based 3D printing process has still not been reported in the scientific literature. In this study, we aim to prepare photosensitive natural rubber (PNR) from NR latex through chemical modification pathways. Subsequently, this modified NR was utilized as a toughness modifier to tune the commercial 3D resin’s properties. The printed part was manufactured using a commercial DLP-type 3D desktop. The mechanical and thermal properties of the printed object were measured. The commercial resin without the addition of modified rubber was also investigated as a control.

2. RESULTS AND DISCUSSION

2.1. Chemical Structure of PNR. Photosensitive natural rubber (PNR) was synthesized by partial epoxidation of natural rubber (NR) followed by degradation reaction to reduce the molecular weight of the rubber before partial addition of acrylic acid to the epoxidized units. The synthesized PNR therefore contained epoxide and acrylate functional groups apart from carbon−carbon double bonds. The molecular structure of NR and PNR was assessed by attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy and proton nuclear magnetic resonance (1H NMR) spectroscopy. ATR-FTIR spectra of rubbers are demonstrated in Figure 1.

![Figure 1. ATR-FTIR spectra of (a) NR and (b) PNR.](image)

NR exhibits notable absorption peaks at 1666 cm$^{-1}$ (C=−C stretching) and 836 cm$^{-1}$ (C−H out-of-plane bending). The absorption peaks at 2924 and 2853 cm$^{-1}$ are attributed to CH$_2$ asymmetric and symmetric stretching vibrations, respectively. Meanwhile, the characteristic peaks at 1445 and 1376 cm$^{-1}$ correspond to CH$_3$ bending vibrations. After chemical modifications, the as-synthesized PNR still shows NR characteristic bands and the appearance of new absorption peaks. The broad peak at 3468 cm$^{-1}$ is assigned to the −OH stretching vibration, obtained from epoxide ring opening after acrylation reaction. Furthermore, PNR displays the characteristics of ester carbonyl stretching (1728 cm$^{-1}$), C=−C stretching of acrylate groups (1641 and 1620 cm$^{-1}$), C=−C bending of acrylate groups (1403 and 810 cm$^{-1}$), and C−O−C of epoxide rings (870 cm$^{-1}$). The 1H NMR technique was also employed to assert the chemical structure of rubbers as illustrated in Figure 2. The NR spectrum shows the main signals at 5.1 (a), 2.03 (a’), and 1.67 ppm (a’’), belonging to methine protons attached to C=−C, methylene protons, and methyl protons of isoprene units, respectively. Meanwhile, the synthesized PNR reveals new signals at various positions. The signals of methine protons and methyl protons of epoxide units are detected at 2.73 (b) and 1.35 ppm (b’), respectively. The signals at 9.78 (c’) and 2.14 ppm (c) can be ascribed to the protons of aldehydes and methyl protons of ketone functional groups, respectively, indicating the existence of aldehyde and ketone groups at the chain end after the oxidative degradation.
PNR contents can gradually promote the viscosity of the characteristic. In the case of viscosity, the enhancement of respectively. Meanwhile, the synthesized PNR acquired polydispersity index (PDI) of NR were found to be providing GPC molecular weight distribution curves (Supporting Information Figure S1). The number average molecular weight distribution curves (Supporting Information Figure S2), all resin formulations was measured from ATR-FTIR spectra to create the kinetic behavior.

The double-bond conversion in each PNR/CR formulation prepared resin from $33.22 \text{ mPa s}$ (0 wt % PNR content) toward $578.15 \text{ mPa s}$ (3 wt % PNR content). It could be attributed to the addition of a high-viscosity NR material into the lower-viscosity resin (CR) system. To sum up, it can be explained that the addition of PNR with various contents (0.9 to 3 wt %) into commercial 3D resin could slightly increase the viscosity of the system without a change in the rheological behavior.

### 2.2. Rheological Behaviors

The PNR solution (30 wt % in toluene) in the range of 0–10 wt % (0–3 wt % PNR contents) was mixed with a commercial 3D printing UV-sensitive resin (CR), and the mixing ratio is shown in Table 1. After evaporating toluene, the viscosity and rheological manners of the PNR/CR mixture were studied using a rheometer with a coaxial cylinder shear mode. As a result (Supporting Information Figure S2), all resin formulations demonstrate the Newtonian aspect throughout the given shear rate. It could suggest that PNR contents ranging between 0.9 and 3 wt % do not alter the neat CR’s rheological characteristic. In the case of viscosity, the enhancement of PNR contents can gradually promote the viscosity of the

| PNR solution/CR (wt %) | PNR content (wt %) | C–C conversion (%) | $E^a$ (GPa) | $\sigma^c$ (MPa) | $\epsilon^c$ (%) | impact strength (kJ/m$^2$) | $T_{\text{vis}}^{d}$ (°C) | $T_{\text{char}}^{\text{d}}$ (°C) | $\%\text{char}^{\text{f}}$ |
|------------------------|---------------------|---------------------|--------------|-----------------|-----------------|-------------------------|------------------------|-------------------------|----------------------|
| 0/100                  | 0.0                 | 86.9                | 2.1±0.3      | 52.4±1.1        | 2.2±0.2         | 2.4±0.4                | 350                    | 420, 472               | 14.6                 |
| 3/97                   | 0.9                 | 85.8                | 2.1±0.2      | 50.2±0.6        | 3.1±0.1         | 4.2±0.3                | 326                    | 419, 471               | 13.7                 |
| 5/95                   | 1.5                 | 84.9                | 2.0±0.1      | 49.2±0.4        | 3.5±0.2         | 5.2±0.4                | 295                    | 417, 470               | 13.5                 |
| 7/93                   | 2.1                 | 83.6                | 2.0±0.2      | 44.4±1.5        | 3.0±0.1         | 4.7±0.4                | 295                    | 412, 468               | 12.8                 |
| 10/90                  | 3.0                 | 81.9                | 1.9±0.3      | 41.9±0.5        | 3.0±0.1         | 3.9±0.5                | 294                    | 410, 467               | 12.5                 |

$^a$Tensile modulus. $^b$Tensile strength. $^c$Elongation at break. $^d$Five percent weight loss temperature. $^e$Maximum weight loss rate temperature. $^f$Char yield.

600 s exposure time. The result shows a noticeable decrement in the double bond of acrylate groups (1640, 1621, 1403, and 810 cm$^{-1}$) after the photocuring process, compared to the starting uncured PNR/CR. Furthermore, a prominent increment of C–H stretching (2924 and 2853 cm$^{-1}$) and C–H bending (1445 and 1376 cm$^{-1}$) is also observed, indicating the transformation of unsaturated units of the acrylate groups into saturated groups after the photocuring reaction by UV exposure.

The double-bond conversion in each PNR/CR formulation was measured from ATR-FTIR spectra to create the kinetic profiles. Figure 4 illustrates the typical plot of the double-bond conversion of PNR/CR mixtures versus UV exposure time ranging from 0 to 600 s. The relevant result of double-bond conversion is summarized in Table 1. All resin formulations provided rapid conversions of more than approximately 82% within 15 s. The neat CR (0 wt % PNR) reached approximately 87% conversion, which can be considered as the final conversion or maximum percentage of cross-linking of
this material. It is not surprising to find that the %conversion cannot reach 100% as the molecular chain movement is restricted at a high percentage of cross-linking. It was found that the final double-bond conversion reduced gradually from 87% (neat CR) down to 82% conversion when 3 wt % PNR was included. Additionally, the mixed resin’s photocuring rate compared to the neat CR shifted gradually toward a high-exposure time zone when PNR contents were increased up to 3 wt %.

The double-bond conversion of PNR/CR mixtures with various PNR contents (0–3 wt %) versus UV exposure time ranging from 0 to 600 s is shown in Figure 4. Plots of the double-bond conversion of PNR/CR mixtures with various PNR contents (0–3 wt %) versus UV exposure time ranging from 0 to 600 s.

Figure 4. Plots of the double-bond conversion of PNR/CR mixtures with various PNR contents (0–3 wt %) versus UV exposure time ranging from 0 to 600 s.

2.4. Mechanical Properties. The PNR/CR mixture resins with various mixing ratios (0–3 wt % rubber contents) were printed into tensile and impact specimens with a dimension according to ASTM D638 and ASTM D256, respectively, using a DLP-type desktop with a 405 nm light source and 12 min exposure time per layer. The uniaxial tensile properties of the printed samples after the UV post-curing process are shown in Figure 5 and summarized in Table 1. The neat CR resin (0 wt % PNR) revealed a typical rigid material having a high modulus (2.1 GPa) and high strength (52.4 MPa) with low stretchability (2.2%). The addition of PNR into the CR resin provided the increment in elongation ability of the printed part from 2.2% (0 wt % PNR) toward the maximum value at 3.5% (1.5 wt % PNR content), an approximately 59% increase when compared to that of the neat CR. Afterward, there is a gradual decline downward to 3.0% with the addition of rubber contents up to 3 wt %. Nevertheless, the strain at break value is still higher than that of the neat CR. The decreasing tendency of the elongation ability after adding more than 1.5 wt % PNR could suggest that the higher amount of rubber content may encourage the possibility of interpenetrating networks, hence restricting the chain mobility. It can be also suggested that a high amount of PNR may induce coalescence of the rubber phase in the resin matrix, resulting in the poor dispersion and distribution of the dispersed rubber phase in the printed part. This forecast can be ensured by morphological analysis discussed in the latter section. In addition, it is not surprising to find that the Young’s modulus and strength of the printed materials were concurrently decreased with addition of the soft PNR material. Young’s moduli decrease slightly from 2.1 GPa (0 wt % PNR) to 1.9 GPa (3 wt % PNR content). Likewise, the uniaxial tensile strengths drop gradually from 52.4 MPa of the neat CR to 41.9 MPa of the PNR/CR containing 3 wt % rubber content. These phenomena could elucidate that PNR as a photosensitive elastomeric material could significantly improve the ductility of the printed samples. However, the decline in the modulus and strength may be due to the rubber’s elastomeric nature and different molecular weights between rubber and the resin matrix. Furthermore, another reason could be that the long polymeric chains of PNR could hinder the segmental reactive-radical movement of growing polymeric chains for collision with the unreacted acrylate groups under the photocuring process.

Figure 5. Tensile properties of the printed PNR/CR resin with various PNR contents (0 to 3 wt %).

Table 1. Tensile properties of printed PNR/CR resins with various rubber contents...

Leading to higher rigidity and strength of the material after UV post-curing than the sample at the green state.
process.\textsuperscript{27} It results in the lowered-cross-linking level of the printed samples after the UV post-curing process when increasing the rubber content. This explanation is consistent with the gel content results of the printed sample after the UV post-curing process, which can be related to the cross-linking degree as presented in Figure 6. The gel content of the neat CR (0 wt % PNR) reaches 98.3\%, indicating the typical high cross-linking network of the material. Nevertheless, there is a gradual decline in the gel content when PNR contents are added into the neat CR resin. The insoluble components reduce from 98.3\% of the neat CR to 93.2\% (3 wt % PNR content), attributed to the decrease in the cross-linking density of the printed part by introducing rubber. To sum up, the decrement of the cross-linking level influences the deterioration of stiffness and strength of the materials.\textsuperscript{3,40} The cross-linking degree can be estimated from the gel content results. Figure 6 compares the gel content of the printed sample after printing and washing (green) and after the UV post-curing process (UV post-cured).

The impact strength of the printed PNR/CR after the UV post-curing process was assessed according to ASTM D256 to attribute the effect of the PNR content on the fracture resistance. Figure 7 illustrates the impact resistance of the printed material, and the values are listed in Table 1. The addition of PNR can promote the impact strength value from 2.4 kJ/m\textsuperscript{2} (0 wt % PNR) to the maximum value at 5.2 kJ/m\textsuperscript{2} of PNR/CR containing 1.5 wt % rubber content. Afterward, the impact strength values reduce to 3.9 kJ/m\textsuperscript{2} when increasing the rubber content up to 3 wt %. This result can be described as that the rubber can behave as a stress raiser for dissipating and absorbing forces received from external sources, resulting in the delay of initiating and propagating processes of failure. The interaction of the rubber and resin matrix could occur via the radical chain transfer and radical coupling between the C=\text{C} bonds of the rubber chains, between the acrylate functional groups attached on the rubber chains, and acrylate functional groups of the CR resin during radical photopolymerization, leading to an increase in the fracture resistance of the material. Furthermore, H-bonding between the hydroxyl groups of PNR and carbonyl of acrylate groups of the resin could be a secondary source of strengthening of the fracture resistance of the products.

Comparing the impact strength of the printed samples containing 1.5 wt % rubber content, the printed PNR/CR having an impact strength of 5.2 kJ/m\textsuperscript{2} is notably higher than the printed L-ENR/CR (2.72 kJ/m\textsuperscript{2}) and neat CR (2.4 kJ/m\textsuperscript{2}) (Supporting Information Figure S5). This result could be raised to confirm the important role of acrylate groups attached in the PNR chains for contributing to the interaction of the rubber and resin matrix via a radical-photopolymerization process of acrylate functional groups.

2.5. Morphological Study. The phase morphologies of the printed PNR/CR at various PNR components (0–3 wt %) were observed from the impact-fractured surface by SEM analysis (Figure 8). The neat CR exhibits a smooth and homogeneous surface (Figure 8a). By adding the as-synthesized PNR as a toughness modifier, the impact-fractured surfaces of all printed PNR/CR show a heterogeneous surface with the dispersed PNR particles in the CR matrix. The dispersed rubber phase can act as a stress raiser to retard the initiating and propagating fracture process after receiving the external force. This typical phase morphology is consistent with the previous work reported by Zareanshahraki et al.\textsuperscript{41} They suggested the formation of dispersed phase particles of poly(dimethyloxiloxane) in a UV-curable acrylate siloxane polymer blend system. Furthermore, considering PNR
contents’ influence, the increase in the rubber content from 0.9 to 3 wt % in the resin matrix provides the increase in dispersed rubber diameter (Figure 8b–e). This phenomenon illustrates the coalescence of the rubber phase when increasing the rubber contents in the resin matrix. Theoretically, a poor dispersion and distribution of the second phase in the polymer blend provide the prepared material with poor mechanical performance. Consequently, this reason was employed to elucidate why the elongation ability and impact resistance of the printed PNR/CR samples were reduced by adding a large quantity of rubber components.

2.6. Thermal Properties. The heat resistance and glass transition temperature \( T_g \) of the printed PNR/CR after the UV post-curing process were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. Figure 9 displays the printed samples’ thermal decomposition, and their relevant degradation temperatures are summarized in Table 1. The thermal decomposition process of the PNR yields a 5% weight loss temperature \( T_{	ext{5\%}} \) of 237 °C and a temperature at the maximum weight loss rate \( T_{	ext{max}} \) of 415 °C without the char yield. The printed PNR/CR samples comprise three stages of the thermal degradation process. The first stage (\(<350 \degree C\)) is the removal of trapped volatile materials, unreacted acrylate moieties, and low-molecular fragmentation. The second stage (350–450 °C) could be attributed to the degradation of the cross-linked polymeric side chains. Meanwhile, the third stage (450–500 °C) could be the decomposition of the cross-linked polymeric main chains of the printed specimen. As for the char yields, about 12–14% is observed. When considering the effect of PNR on the neat CR’s thermal resistance, there is a slight decrement in \( T_{	ext{5\%}} \) and \( T_{	ext{max}} \) when PNR contents increase from 0.9 to 3 wt %. As a result, the decline in thermal resistance by incorporating the modified NR could be attributed to the decrement in the material’s cross-linking density. Consequently, it is consistent with the deterioration of tensile strength and gel contents. Voet et al. also suggested that the printed material with a higher cross-linking density provided a higher Young’s modulus, mechanical strength, and thermal stability.

The glass transition-relaxation manners of the printed PNR/CR after the UV post-curing process measured by DSC analysis are demonstrated in Figure 1. The \( T_g \) of the synthesized PNR is approximately −50 °C (Supporting Information Figure S6). DSC thermograms of the printed PNR/CR samples in Figure 10 illustrate two glass transition-relaxation points at the low-temperature zone (−38 to −31 °C) and high-temperature zone (60 to 69 °C), corresponding to the \( T_g \) values of the rubber phase and the CR matrix, respectively. The glass transition peaks of the rubber phase seem to be small. This result may be due to the small amount of the PNR content. Another reason is the rubber molecular motion’s restriction after the cross-linking process, and thus, the \( T_g \) of the cross-linked rubber fraction in this work was not easily detected by DSC measurement. Additionally, there is a shift in \( T_g \) of the prepared PNR (−50 °C) upward to a higher temperature between −38 and −31 °C for PNR/CR with various rubber contents (0.9 to 3 wt %). This phenomenon could indicate that the segmental chain motion of PNR is restricted due to the cross-linking and interpenetrating network formations of PNR/CR after the UV curing process. There is a noticeable shift in \( T_g \) of the neat CR (69 °C) downward to a lower temperature between 68 °C (0.9 wt % PNR) and 61 °C (3 wt % PNR). Two rationales may be illustrated for this tendency. First, the PNR-CR network formation may suggest the decline in \( T_g \) of the matrix phase. Second, the \( T_g \) of the UV-curable material is generally relative to the cross-linking level. A high cross-linking degree provides the material with a high \( T_g \) value. As a result, the addition of PNR could reduce the cross-linking network density of the printed sample and decrease more with increasing rubber contents. Therefore, the decline in \( T_g \) of the printed PNR/CR was observed in this work.

Figure 9. Thermal decomposition temperature of the printed PNR/CR with various PNR contents (0 to 3 wt %).

Figure 8. SEM images of the impact-fractured surface of printed PNR/CR with various PNR contents: (a) 0, (b) 0.9, (c) 1.5, (d) 2.1, and (e) 3 wt % PNR.

Table 1. Thermal decomposition temperature of the printed PNR/CR after the UV post-curing process measured by DSC analysis.
3. CONCLUSIONS
Photosensitive natural rubber (PNR) was successfully prepared by chemical modifications of NR with incorporation of acrylate groups. The synthesized PNR (0−3 wt %) was mechanically mixed with a commercial 3D resin (CR) for the UV-curable additive manufacturing process. The viscosities of resins slightly increase with the addition of the modified rubbers without a change in the rheological behavior. The successful printed test specimen with a DLP 3D printer demonstrated a significant increase in the elongation ability and impact performance of the printed PNR/CR objects with additional rubber content toward 1.5 wt %. The synthesized PNR can act as a stress concentrator to dissipate energy, delaying the fracture process. Meanwhile, there is a slight decrement in the Young’s modulus, strength, and gel content as well as thermal stabilities with the addition of the modified rubber. Phase morphology of the printed parts revealed a heterogeneous surface having the rubber droplets dispersed in the CR matrix. Additionally, the shift in \( T_g \) of the rubber and the matrix could elucidate the existence of cross-linking network formations between the rubber and CR matrix. Consequently, this work demonstrates the utilization of photosensitive natural rubber as an impact modifier in UV-curable resin applied for the light-based 3D printing process. It can be noted that the mixed resin consisted of approximately 0.9−3.0 wt % renewable natural rubber, which is the modified rubber in the blended resins. The benefit of this work is the extension of the utilization of NR, found abundantly in Asian countries, with high value added for application in the additive manufacturing process.

4. EXPERIMENTAL SECTION

4.1. Materials. NR latex (60% dried rubber content), was purchased from Thai Rubber Latex Co., Ltd. (Thailand). Tergitol 15-S-15 (nonionic surfactant) was procured from Sigma Aldrich (USA). Hydrogen peroxide (35% w/w) was supplied by QRec (New Zealand). Formic acid (85% w/w) was bought from Carlo Erba Reagent (USA). Periodic acid (99%) was received from Shanghai Runwu Chemical Technology Co., Ltd. (China). Acrylic acid (99%) was provided by Shandong Sparrow Chemical Co., Ltd. (China). A commercially available 3D printing UV-sensitive resin (CR) with the trade name “ANYCUBIC” was purchased from Shenzhen Anyucubic Technology Co., Ltd. (China). The composition of the CR according to the safety data sheet (SDS) revealed a typical acrylate-based resin containing polyurethane acrylate (30−60%), an acrylate monomer (10−40%), and a photoinitiator (2−5%).

4.2. Preparation of Photosensitive Natural Rubber (PNR). NR latex as a raw material was chemically modified to produce the synthesized PNR through three steps in the following chemical pathways: epoxidation, oxidative degradation, and acrylation reactions as schematized in Scheme 1.

First, stabilized NR latex was prepared by adding 3 phr (3.6 g) of tergitol 15-S-15 as a nonionic surfactant into 600 mL of NR latex (20% dry rubber content) with stirring at room temperature for 24 h. Subsequently, the epoxidation of NR was carried out by simultaneously adding 1 mol (154 mL) of hydrogen peroxide and 0.25 mol (22 mL) of formic acid into the stabilized NR latex. The reaction mixture was agitated over 3 h at 60 °C to gain the epoxidized NR (ENR) latex. Then, the ENR latex was cooled down to room temperature (25 ± 2 °C) followed by adjustment of pH to 7 by an ammonium hydroxide solution. Afterward, an oxidative chain degradation utilizing periodic acid as an oxidizing agent was carried out to produce the low-molecular-weight epoxidized natural rubber (L-ENR). One mole (180 g) of periodic acid was introduced into the ENR latex and stirred continuously over 12 h at 40 °C. At the end of the reaction, the prepared L-ENR latex was precipitated by methanol and washed with water several times before drying at 40 °C in a vacuum oven. Subsequently, acrylation reaction was performed as a third step to achieve PNR. L-ENR (20 g) was completely dissolved in 300 mL of...
toluene followed by addition of 3 mol (27 mL) of acrylic acid as a photosensitive acid. The reaction mixture was manipulated over 12 h at 75 °C. At the end of the acrylation reaction, the synthesized PNR solution was precipitated by methanol and washed several times by water before drying at room temperature (25 ± 2 °C) using a vacuum oven.

4.3. Preparation of the PNR/CR Mixture. First, a 30% w/w PNR solution was prepared using toluene as a solvent. Then, the PNR solution was mixed with CR at various ratios ranging from 3 to 10 wt % PNR solution contents (0.9 to 3 wt % PNR content). The PNR solution/CR mixture was mechanically stirred with 600 rpm rotational speed for 1 h at room temperature (25 ± 2 °C) until the mixture resin is homogeneous. Afterward, the mixture resin was sonicated in an ultrasonic bath (40 kHz and 50 W) for 30 min in a fume hood for dispersing PNR in the resin and evaporating toluene in the mixture resin at room temperature (25 ± 2 °C). Finally, the residual toluene solvent and some air bubbles within the mixture resin were eliminated using a vacuum oven for 3 min at room temperature. The bubble-free PNR/CR resin was kept in a dark room for utilization in the light-based 3D printing process.

4.4. Fabrication of the 3D Printing Part. The specimens of PNR/CR mixtures were fabricated using a Sparkmarker (SK-US01, China) as a DLP-type desktop with a 405 nm light source. The printing volume of the 3D printer is 98 × 55 × 125 mm³ with a 100 μm XY resolution and a 25−100 μm Z-axis resolution. Before starting the process, the 3D models of tensile and impact specimens with a dimension according to ASTM D638 and ASTM D256, respectively, were created for dispersing PNR in the resin and evaporating toluene in the mixture resin at room temperature (25 ± 2 °C). Finally, the residual toluene solvent and some air bubbles within the mixture resin were eliminated using a vacuum oven for 3 min at room temperature. The bubble-free PNR/CR resin was kept in a dark room for utilization in the light-based 3D printing process.

4.5. Characterization. The chemical structure of PNR was assessed by 1H NMR using a 500 MHz Ultrashield NMR spectrometer (Bruker). Deuterated chloroform (CDCl₃) was utilized as a solvent.

A Paragon 1000 FTIR spectrometer with an attenuated total reflectance (ATR) accessory (PerkinElmer) was also used to analyze the chemical structure of the PNR. ATR-FTIR spectra were scanned from 4000 to 400 cm⁻¹ with 64 scans and a 4 cm⁻¹ resolution.

Double-bond conversion (DBC) related to the kinetic profiles of samples was determined by ATR-IR mode. The mixture resins before the photocuring process were evaluated as a reference. Meanwhile, the thin sheet (100 ± 5 μm) of the cured PNR/CR was measured at six different positions in each side. DBC values were calculated as presented in eq 3.98

\[
\text{DBC} (\%) = 1 - \left( \frac{A_{\text{uncured at 1403 cm}^{-1}}}{A_{\text{cured at 1403 cm}^{-1}}} \right) \times 100
\]

where \( A_{\text{uncured}} \) and \( A_{\text{cured}} \) are the peak area of uncured and cured samples at 1403 cm⁻¹ (C=O bonding of acrylate groups) and 1728 cm⁻¹ (C≡O stretching of acrylate groups).

Gel permeation chromatography (GPC) was employed to determine the molecular weight of rubbers using a Waters ALC/GPC 150C. Five milligrams of rubber was dissolved in tetrahydrofuran (THF) and then filtered with a 0.22 μm nylon syringe filter before measurement. THF was used as an eluent with a flow rate of 1 mL/min at 40 °C using a guard column (Polymer Laboratories, Styragel@HRSE, 7.8 × 300 mm²) and a refractive index detector (Waters 2414). The weight average molecular weight (\( M_w \)), number average molecular weight, and polydispersity index (PDI) of rubber samples were reported in this measurement.

Rheological behavior revealed the resin viscosity of PNR/CR mixtures measured using a Physica MCR 500 rheometer (Anton Paar) using a coaxial cylinder shear mode. The shear rate was measured in the range of 0.1 to 100 s⁻¹ under room temperature (25 ± 2 °C). Viscosity plotted against the shear rate was demonstrated.

The insoluble fraction or gel content of the printed specimen after washing (green state) and the UV post-curing process was measured by Soxhlet extraction. Fifteen grams of the printed part was extracted with excessive toluene at 130 °C for 24 h. The gel fractions were dried using a vacuum oven to obtain a constant weight. The amount of gel fractions was calculated as shown in eq 4. The average value and standard deviation were significantly determined.

\[
\text{Gel content} (\%) = \frac{\omega_c - \omega_o}{\omega_o} \times 100
\]

where \( \omega_o \) and \( \omega_c \) are the dry weight of samples before and after a Soxhlet extraction, respectively.

Tensile properties were measured using a 5566 universal testing machine (Instron) with a 1 kN static load cell capacity according to ASTM D638. Ten printed specimens of each sample were measured with a crosshead speed of 10 mm/min at room temperature (25 ± 2 °C). The Young’s modulus, tensile strength, and elongation at break of printed parts were achieved.

Impact properties were measured using a 5102 Pendulum impact tester (Zwick) by conforming to ASTM D256. Eight printed notched impact specimens of each sample were investigated under Izod mode at room temperature (25 ± 2 °C). The impact strength was reported in kJ/m² units.

Scanning electron microscopy (SEM) was employed to observe the surface morphology of the printed sample and performed using an SU 8000 (Hitachi). The impact-fractured surface was coated with platinum/palladium (Pt/Pd) before observation.

A thermogravimetric analyzer (TGA), Mettler QS00 (TA Corporation), was utilized to measure thermal resistance of the printed objects. Testing of 10 mg of samples was performed using a 10 °C/min heating rate with the temperature profile between 40 and 500 °C under a nitrogen atmosphere.

Differential scanning calorimetry (DSC) using a DSC 7 (PerkinElmer) was employed to obtain the glass transition temperature (\( T_g \)) of the rubbers and the printed samples.
Testing of 10 mg of samples proceeded with a heat–cool–heat scan at a 10 °C/min heating rate starting from −80 to 120 °C.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00418.

Additional GPC results; rheological data; kinetic profiles of CR, L-ENR/CR, and the PNR/CR mixture; functional group conversion, mechanical properties, and DSC thermograms of different types of rubbers (PDF)

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**Notes**

The authors declare no competing financial interest.

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