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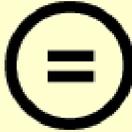
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Master's Thesis

Ultraviolet-curable Silicone/Urethane Elastomer
and Its Selective Modulus Enhancement

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2018

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A thesis submitted to the Graduate School of UNIST
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07/09/2018

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Abstract

Thermosets usually have brittle structure, but thermosetting polyurethane (PU) is classified as elastomer due to its urethane linkage in the backbone. Polyurethanes are used in many areas in a form of foam, adhesive and especially as an elastomer. To utilize elastomers in various applications without being fractured, various methods to control the mechanical properties of elastomers have been investigated such as incorporating fillers and additives or creating multiple networks. In this study, ultraviolet-curable silicone containing polyurethane acrylate was synthesized from poly(tetrahydrofuran) (PTH), hydroxy-terminated poly(dimethyl siloxane) (PDMS) and isophorone diisocyanate. The polyurethane chain was terminated with acrylate to fabricate modulus tunable and rapidly crosslinkable silicone/urethane composite elastomer. By adding 3-(trimethoxysilyl)propyl acrylate to the silicone/urethane elastomer network, the mechanical properties of silicone/urethane elastomer can be enhanced by creating additional covalent bonds at elevated temperature. The mechanical properties of the silicone-contained PUA elastomer can be enhanced even after complete photopolymerization, and local modulus enhancement is also possible by heating only desired area of the elastomer. We believe that the silicone/urethane elastomer can be used to fabricate flexible devices, force sensor, etc.

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Table 1. Synthesized PUA resins while varying the molecular weight of PTH, the ratio of PTH to PDMS and synthesis temperature.

Table 2. Young's modulus (E) of each PUA elastomers.

Nomenclature

PUA	Polyurethane acrylate
PUA_{a-b-c}	PUA synthesized from PTH having a number average molecular weight of a g/mol and PDMS, with a molar ratio of PTH:PDMS=1:0 (b=0) or 4:1 (b=1) at a temperature of c (°C)
PTH	Poly(tetrahydrofuran)
PTH_d	PTH having a number average molecular weight of d g/mol
PDMS	Poly(dimethylsiloxane)
IPDI	Isophorone diisocyanate
DBTDL	Dibutyltin dilaurate
HEA	2-Hydroxyethyl acrylate
THF	Tetrahydrofuran
GPC	Gel permeation chromatography

I. INTRODUCTION

1.1 Polyurethane acrylate

Polyurethanes are made by the exothermic reactions between di(or poly)ol with di(or poly)isocyanate and make urethane linkages. Urethane bonds in the backbone make the polyurethane classified as elastomer. The properties of resulted polyurethane are affected by which kind of alcohol or isocyanate monomers were used, the ratio of isocyanate to hydroxyl groups and the type of chain extender (Sung, G., et al., 2016; Rahman, M. M., et al., 2009; Du, H., et al., 2008; Rahman, M. M., et al., 2006; Somani, K.P., et al., 2003). Since polyurethane-based elastomers have excellent mechanical and thermophysical properties such as high tensile strength, large reversible elongation, and enhanced rubbery modulus, polyurethane is generally used in many different areas in various forms including foam, elastomer, adhesive, etc (Figure 1). The mechanical properties of polyurethane elastomer itself and polyurethane blends were studied thoroughly (Eceiza, A., et al., 2008; Kojio, K. et al., 2007; Prisacariu, C. et al., 2005; Chang, Z. et al., 2013; Xiao, D. et al., 2010), as well as that of other elastomeric materials containing urethane moieties as an enhancement (Suresh S. N., et al., 2007; Fu, B. X., et al., 2000; Chen S., et al., 2012; Feng, F. et al., 2011) (Figure 2). Eceiza et al. studied the effect of molecular weight and chemical structure of diol, and how much the monomer segments are soft or hard on the thermal and mechanical properties of thermoplastic polyurethane elastomers. In other literature, the effects of a relative amount of hydroxyl groups to isocyanate groups and the content of enhancer on the mechanical properties of elastomers were also investigated.

1.2 Mechanical Properties Enhancement of Polymeric Elastomer

Since it is important for polymeric elastomers not to fracture at low stress or strain, various methods were investigated to enhance the mechanical properties of elastomers (Figure 3). To improve the mechanical strength of elastomers, nanocomposites or fillers such as graphene, cellulose nanocrystals, silver nanowires, iron oxides, calcium carbonate, fiber, glass microspheres can be incorporated into polymer matrix (Aihua P., et al, 2011; Shanmugaraj, A. M. et al., 2007; Pingan, S., et al., 2011; Pradhan, S. et al., 2008; Pinto, U.A.

et al., 2001; Nunes, R. C. R. et al., 1999; Pukanszky, N., 1990; Bigg, D. M., 1987; Edwards, D. C., 1990; Yuan, Q. et al., 1999; Mi, H. Y. et al., 2014; Mohammadi, A. et al., 2013; Wang, H. et al., 2008; Jiang, L. et al., 2006; Im, H. et al., 2011), additives like POSS can be mixed in pre-polymer solution (Bruce X. F., et al., 2000; Zhen, Z., et al., 2015; Qinglei, Z., et al., 2016; Kojio, K. et al., 2009;) or creating multiple networks (Du, W., et al., 2018; Ducrot, E., et al., 2014; Lin, Y., et al., 2016; Wang, W. et al, 2017; Wang, R. et al, 2015; Pervin, R. et al., 2015) which can enhance the overall mechanical properties and also be used as sacrificial bonds.

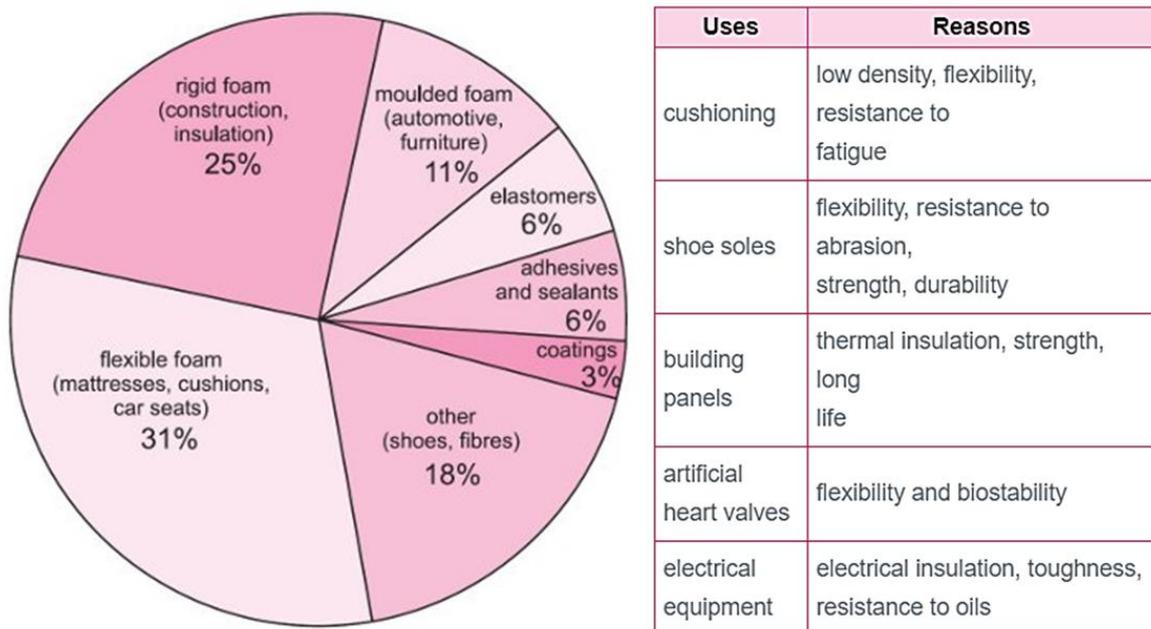


Figure 1. General uses and properties of polyurethane.

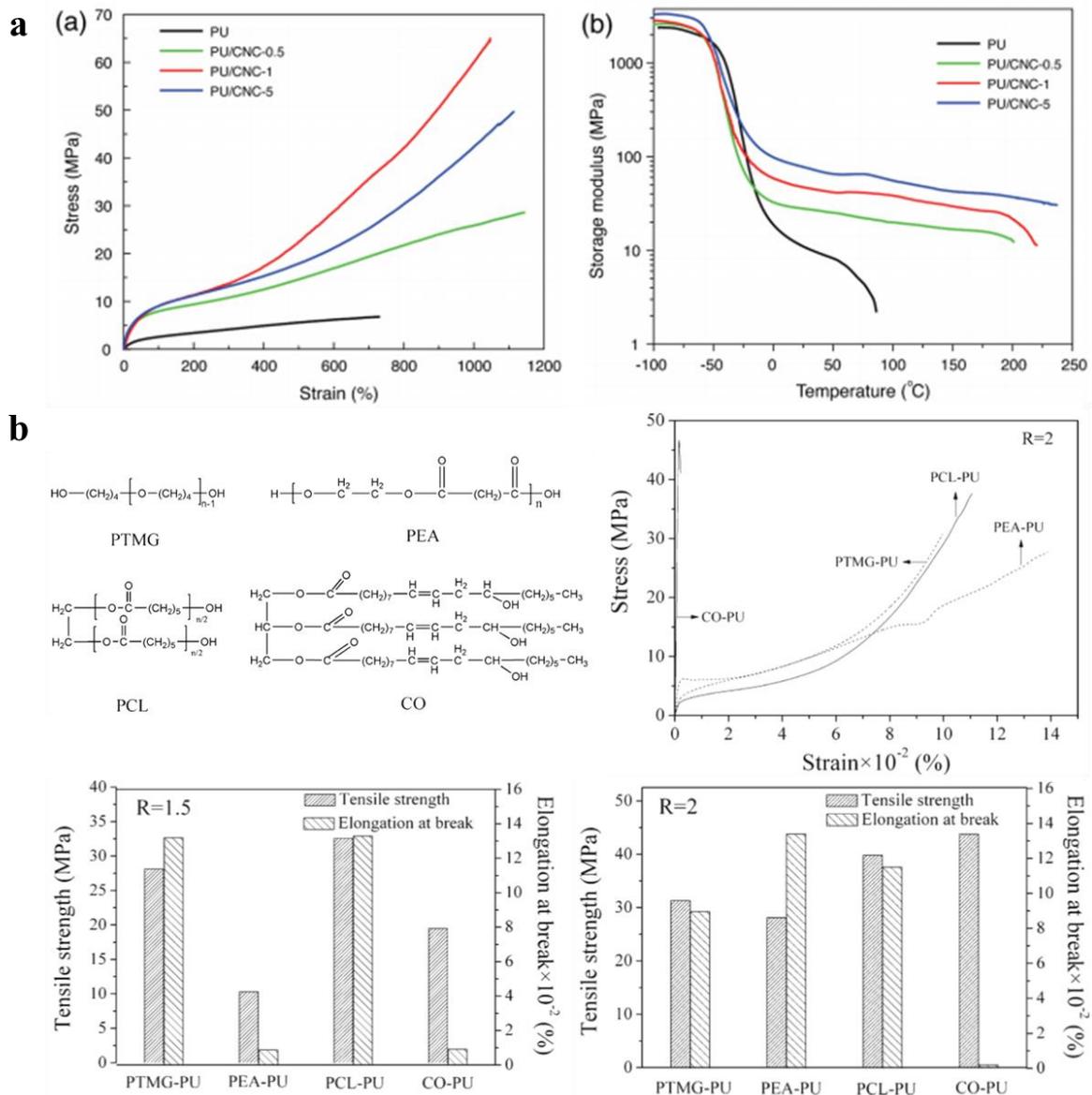


Figure 2. (a) Stress-strain curves of pure polyurethane (PU) and PU/cellulose nanocrystal (CNC) nanocomposites and storage modulus of the PU and PU/CNC nanocomposites as a function of temperature (Aihua P., et al., 2011). (b) Chemical structures of the polymer polyols, Stress-strain curves of the various PU with isocyanate index (R) is 2 and tensile properties of PU based on various polyols with R is 1.5 and 2 (Chen, S., et al., 2012).

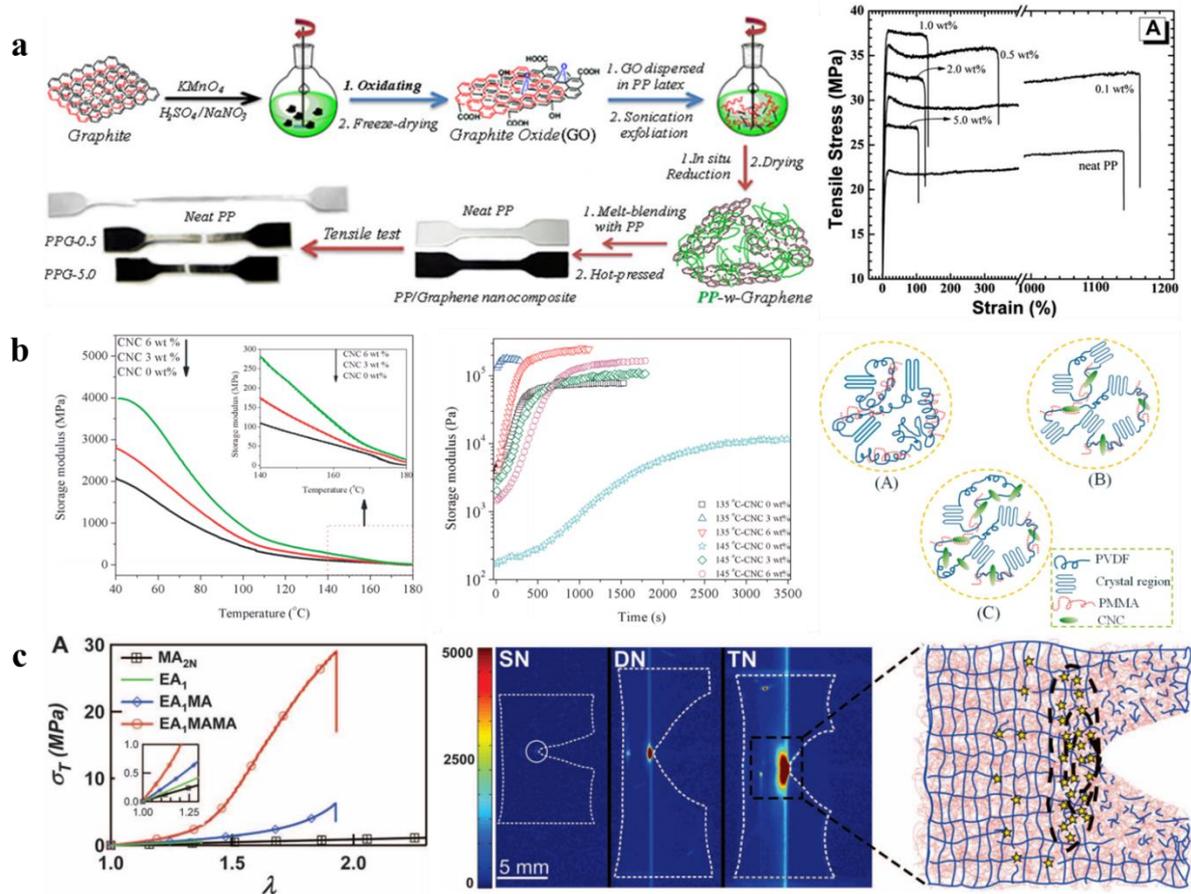


Figure 3. Various methods to enhance the mechanical properties of polymeric elastomers. (a) Schematic representation of process flow of polypropylene (PP)/graphene nanocomposites fabrication and representative stress-strain behavior of PP/graphene nanocomposites with various graphene loadings (Pingan, S., et al., 2011). (b) Storage modulus, time evolution of storage modulus and schematic representation of the mechanism for the improved performance for PVDF/PMMA blend and its composites (Zhen, Z., et al., 2015). (c) True stress/stretch curve and crack propagation mapping for single network (SN), double network (DN) and triple network (TN) samples (Ducrot, E., et al., 2014).

1.3 Research Motivation

Although there are various methods to enhance the mechanical properties of elastomers, incorporation of other materials such as nanocomposites, fillers and additives to the polymeric matrix might not be the best way for mechanical properties enhancement. In order to improve the mechanical properties using nanocomposites, fillers or additives, their surfaces should be treated in a way of ensuring high affinity to the polymeric matrix (Ning, N. et al., 2012; Khoshkava, V. et al., 2013). Otherwise, incorporated materials would be easily separated from the matrix, make cracks and eventually result in failure of the elastomer rather than enhancing the material's mechanical properties (Naeim A. A. et al., 2017; Jouault, N. et al., 2009). Even if it is possible to ensure the high affinity of the fillers to the polymeric matrix, there are some additional steps needed to prepare their surfaces in a way that they can be incorporated well in the matrix. In case of creating additional bonds or networks in a polymer matrix, it is hard to tune the mechanical properties while not changing the composition of prepolymer solution. Thus, it is important to develop a method which is simple yet gives enough mechanical property enhancement of elastomers and desired extent of enhancement.

1.4 Research Objective

We aimed to develop a novel method to enhance the mechanical properties of polyurethane elastomers in a selective area while adjusting the extent of enhancement, even after the complete photo-curing. To realize the goal, two kinds of diol were used to synthesize polyurethane resin: poly(tetrahydrofuran) (PTH) and hydroxy terminated poly(dimethylsiloxane) (PDMS). Enhancing the mechanical properties of elastomers in a selective region was done by forming additional Si-O covalent bond simply by baking or heating desired area of the PUA elastomer. Selectively enhanced mechanical strength of PUA elastomers was verified by observing deformation of a spot drawn on a surface of the elastomer and resistance change of Pt layer on the surface of the elastomer.

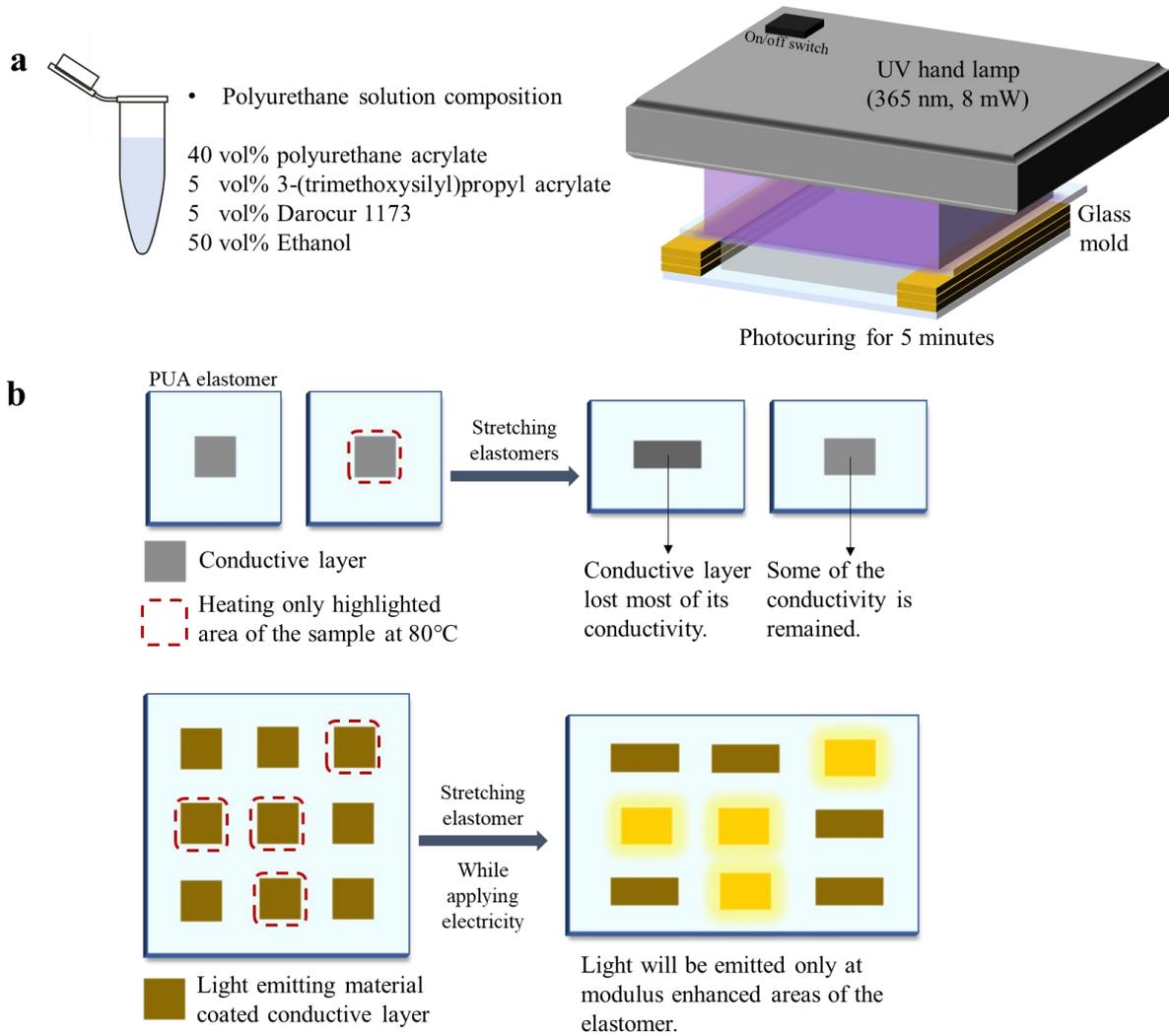


Figure 4. (a) The composition of polyurethane prepolymer solution and its photocuring conditions. (b) The schematic view of research objective.

II. EXPERIMENTAL SECTION

2.1 Materials

Poly(tetrahydrofuran) (PTH, M_n 650 g/mol, M_n 2000 g/mol), hydroxyl terminated poly(dimethylsiloxane) (PDMS, M_n 550 g/mol), isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), anhydrous 2-methyl-1-propanol, hydroxyethyl acrylate (HEA) and 2-hydroxy-2-methylpropiophenone (Darocur 1173) were purchased from Sigma-Aldrich. 3-(trimethoxysilyl)propyl acrylate was purchased from TCI Chemicals. All purchased chemicals were used as received. Tetrahydrofuran (THF) was distilled from sodium/benzophenone within a day before synthesis to prepare anhydrous THF.

2.2 PUA synthesis

The procedure was modified from an existing journal (Le H. S., et al, 2016). A mixture of 2 g IPDI and 0.1098 g DBTDL (1wt%) in 10 mL of anhydrous THF was fed into a 100 mL three-neck flask. Nitrogen bubbling was carried out for 30 min to introduce inert environment. The mixture was heated to 60°C (or 50°C). A mixture of 7.1981 g PTH (M_n 650 g/mol or 2000 g/mol) and 0.494 g PDMS in 35 mL anhydrous THF was added slowly in 1 h to reaction flask. The reaction was carried out for another 2.5 h at 60°C (or 50°C) with Nitrogen flow. A mixture of 0.8197 g HEA and 0.1996 g 2-methyl-1 propanol in 5 mL anhydrous THF was added and the reaction was continued for another 1 h. Solution of 0.2668 g of 2-methyl-1-propanol in 1 mL anhydrous THF was added and stirred another 30 min to terminate the polymerization reaction. Finally, anhydrous THF was evaporated by using a rotary evaporator and the liquid colorless resin was obtained after extraction with mixture diethyl ether and hexane at a ratio between 5:3 and 1:1. The resin was stored in cool dark place to avoid crosslink reaction during storage.

2.3 PUA elastomer fabrication

A weighted PUA resin (40 wt%) was fed into an Eppendorf tube. 3-(trimethoxysilyl)propyl acrylate (5 wt%) and ethanol (50 wt%) were added to the tube. Place

the tube in a shaker for at least 3 hours to ensure that the PUA resin is fully dissolved in ethanol. Darocur 1173 was added to the mixture and the mixture was finally mixed for 30 minutes. The mixture was degassed before filling the mold. While degassing, a mold was prepared with two sheets of slide glass as bottom or top and polyimide tape was used as a 500 μm thick spacer. The mold was filled with the mixture and UV-cured using UV hand-held lamp (8 mW) for 5 minutes. After UV curing, PUA elastomer was soaked in ethanol to remove uncured resin. This step was repeated two times more with fresh ethanol and then the elastomer was dried in air. To tune the mechanical properties of the elastomer, desired area of the elastomer was heated at 80°C for one or two hours. The size of the prepared samples was 7 mm*25 mm*0.4 mm and 19 mm*19 mm*0.4 mm for tensile test and resistance tuning test, respectively.

2.4 Characterization

FT-NMR spectroscopy was performed on a 400 MHz Avance III HD (Bruker) using deuterated chloroform (CDCl_3) as a solvent to ensure the synthesized product is a desired one. Gel permeation chromatography (GPC) was carried out on an Agilent 1200S/miniDAWN TREOS (Agilent/Wyatt) using tetrahydrofuran as eluent. Viscosity of resin was evaluated on a Haake MARS III - ORM Package (Thermoelectron). Mechanical properties of PUA elastomers were investigated on Instron universal testing equipment with speed of 10 mm/min.

III. RESULTS AND DISCUSSION

3.1 PUA synthesis

Poly(tetrahydrofuran (PTH) and poly(dimethylsiloxane) PDMS were selected as alcohol monomers which are relatively soft segments, and isophorone diisocyanate (IPDI) was selected as isophorone monomers which are relatively hard segments (Figure 5). Urethane bond in a main chain gives polymer sufficient flexibility and elasticity, and Si-O bond in PDMS segments provides additional elastic property to the PUA polymer chain. To prepare photocurable polyurethane resin, the polymer chain was terminated using hydroxyethyl acrylate (HEA). HEA has higher reactivity than hydroxyethyl methacrylate (HEMA) (Lee, T. Y. et al., 2004), thus terminating chain with HEA rather than HEMA enables faster photopolymerization under UV light having the same intensity in the presence of an appropriate photoinitiator. 2-Methyl-1-propanol was also used to terminate the polymer chain, and 2-methyl-1-propanol-terminated chain end does not have reactivity under UV light in the presence of a photoinitiator. The methyl terminated chain acts as a kind of plasticizer which inhibits the polymer chains from tightly packed or entangled each other and drops the viscosity of PUA resin. Three variables were concerned as synthesizing various types of PUA resin: the molecular weight of PTH, the ratio of PTH to PDMS and synthesis temperature (Table 1).

Table 1. Synthesized PUA resins while varying the molecular weight of PTH, the ratio of PTH to PDMS and synthesis temperature.

PUA _{xx-x-xx}	PUA 650-0-50	PUA 650-0-60	PUA 650-1-50	PUA 650-1-60	PUA 2000-0-50	PUA 2000-0-60	PUA 2000-1-50	PUA 2000-1-60
M _n of PTH (g/mol)	650	650	650	650	2000	2000	2000	2000
PTH:PDMS (molar ratio)	1:0	1:0	4:1	4:1	1:0	1:0	4:1	4:1
Synthesis temperature	50°C	60°C	50°C	60°C	50°C	60°C	50°C	60°C

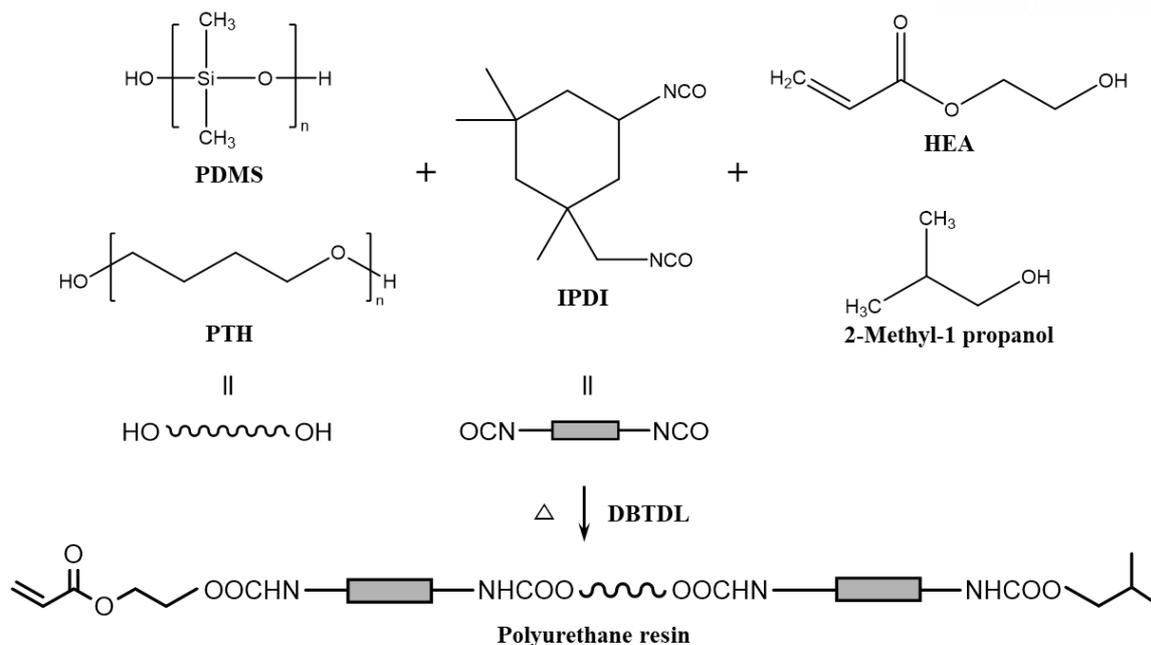


Figure 5. Synthesis of photocurable polyurethane acrylate resin.

The molecular weight of synthesized resin was measured by gel permeation chromatography (GPC) (Figure 6 and Figure 7). While there was almost no difference between the molecular weight of PUA_{650-X-50} and PUA_{650-X-60}, The molecular weight of PUA_{2000-X-60} showed a huge difference from the molecular weight of PUA_{2000-X-50}. There are several reasons which can affect the molecular weight of PUA resins. PTH₆₅₀ has shorter chain, less entanglement and higher solubility in THF than PTH₂₀₀₀. It means PTH₆₅₀ can move more freely than PTH₂₀₀₀ in a PUA reaction mixture even at a lower temperature. The active movement enables higher conversion at relatively low temperature, and it might decrease the difference between a molecular weight of PUA_{650-X-50} and PUA_{650-X-60}. On the other hand, PTH₂₀₀₀ chains are more entangled and do not move as freely as PTH₆₅₀ chains move at the same temperature. Since PTH₂₀₀₀ can move freely at elevated temperature, the reaction conversion is lowered while synthesizing PUA from PTH₂₀₀₀ at relatively low temperature. Thus, there are huge differences between PUAs synthesized from PTH₂₀₀₀ at 50°C and 60°C. In addition, there was almost no difference between the molecular weight of PUA_{650-0-XX} and PUA_{650-1-XX} while there was a big difference between the molecular weight of PUA_{2000-0-XX} and PUA_{2000-1-XX}. The reason is that the molecular weight of PDMS (M_n 550

g/mol) is much lower than PTH₂₀₀₀.

The viscosity of polyurethane resin at a given shear rate was measured using rheometer (Figure 8). The viscosity of pure PUA₆₅₀₋₁₋₅₀, PUA₂₀₀₀₋₁₋₅₀ and PUA₂₀₀₀₋₁₋₆₀ resins at shear rate 250 is 49,000 cP, 80,000 cP and 67,000 cP, respectively. The viscosity of honey at room temperature is 10,000 cP, thus the pure PUA resins are too thick to handle. The resin is diluted with 50 v% ethanol for fabricating PUA elastomers. The composition of a prepolymer solution is 40 v% PUA, 5 v% 3-(trimethoxysilyl)propyl acrylate, 5 v% Darocur 1173 and 50 v% ethanol. The viscosity of PUA₆₅₀₋₁₋₆₀ and PUA₂₀₀₀₋₁₋₆₀ solution at shear rate 250 is 100 cP and 600 cP, respectively (1000 cP = 1 Pa.s).

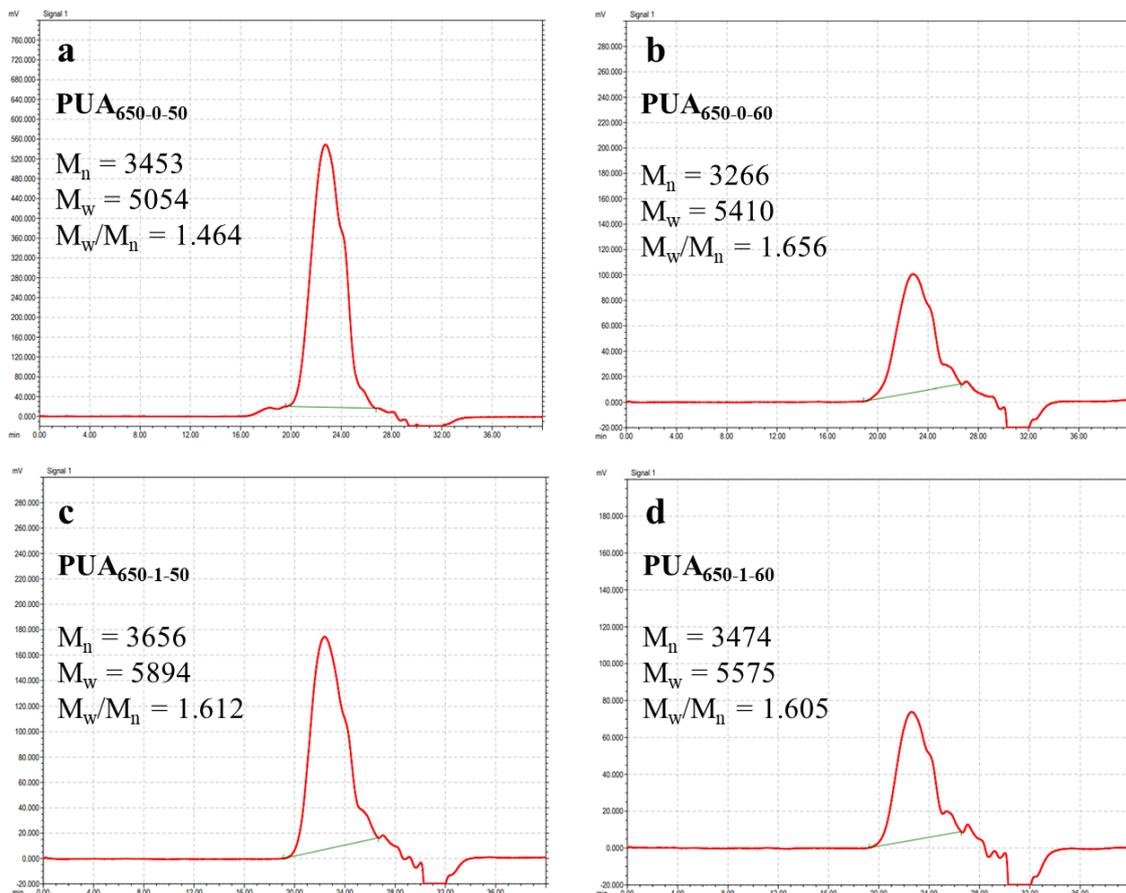


Figure 6. Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of (a) PUA₆₅₀₋₀₋₅₀, (b) PUA₆₅₀₋₀₋₆₀, (c) PUA₆₅₀₋₁₋₅₀ and (d) PUA₆₅₀₋₁₋₆₀.

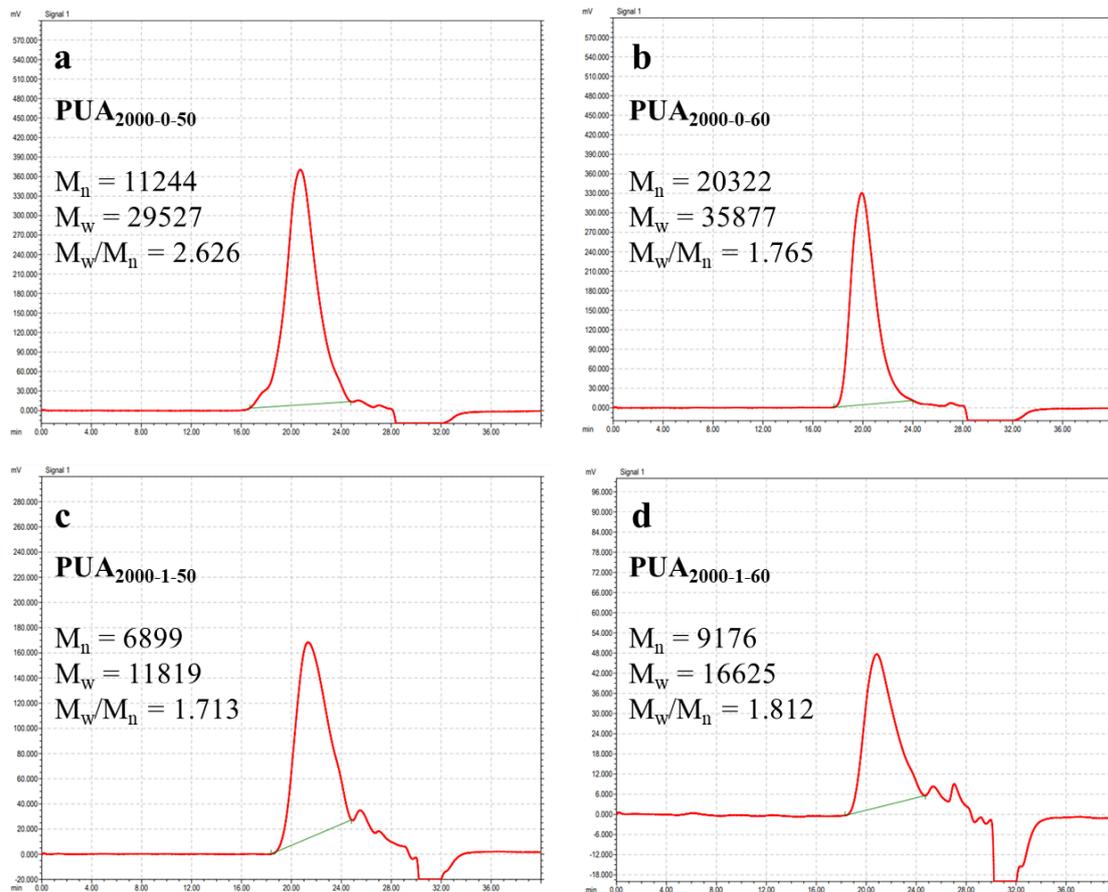


Figure 7. Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of (a) PUA₂₀₀₀₋₀₋₅₀, (b) PUA₂₀₀₀₋₀₋₆₀, (c) PUA₂₀₀₀₋₁₋₅₀ and (d) PUA₂₀₀₀₋₁₋₆₀.

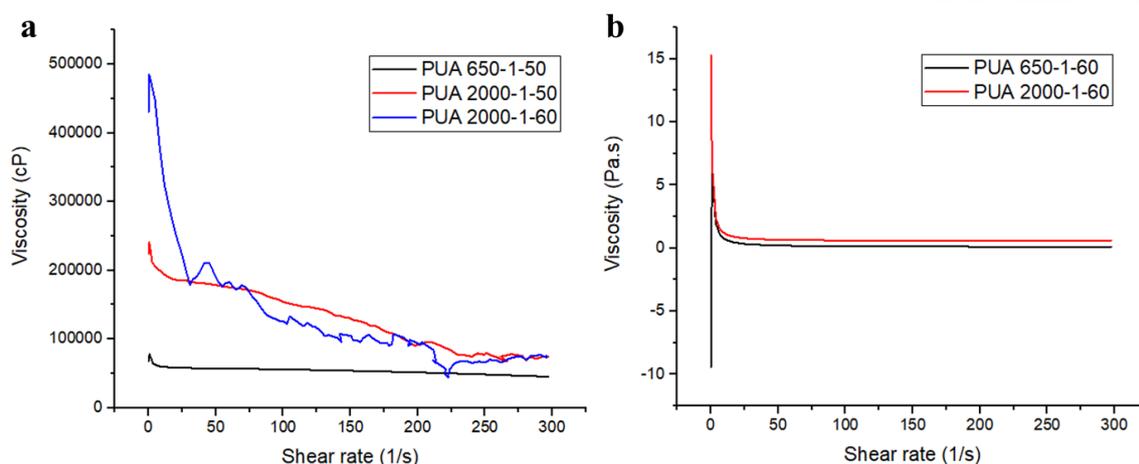


Figure 8. (a) The viscosity of pure polyurethane resin at a given shear rate. The viscosity of PUA₆₅₀₋₁₋₅₀, PUA₂₀₀₀₋₁₋₅₀ and PUA₂₀₀₀₋₁₋₆₀ at shear rate 250 is 49,000 cP, 80,000 cP and 67,000 cP, respectively. (b) The viscosity of prepolymer solution (40 v% PUA, 5 v% 3-(trimethoxysilyl)propyl acrylate, 5 v% Darocur 1173 and 50 v% ethanol) at a given shear rate. The viscosity of PUA₆₅₀₋₁₋₆₀ solution and PUA₂₀₀₀₋₁₋₆₀ solution at shear rate 250 is 100 cP and 600 cP, respectively (1000 cP = 1 Pa.s).

3.2 Tensile test

For exact measurement of the mechanical properties, PUA elastomers should be in a dumbbell shape. PUA synthesized using only PTH as diol monomers and PUA synthesized using the mixture of PTH and PDMS in a ratio of 3 to 1 were used to prepare tensile test specimens (Figure 9). All of the samples were prepared by cutting edges in a dumbbell shape manually with a blade. Since the edge of the specimens were rough and had minor cracks, the samples were fractured earlier than they were supposed to be, so we could not measure exact elongation at break. However, we could obtain reasonable data for modulus of each sample through the test.

Because of early fracture of manually cut samples, we decided to use PDMS molds or a photomask instead of cutting with a blade. The dumbbell shaped PDMS elastomers made from PUA₂₀₀₀₋₁₋₆₀ were fabricated using mold A, B, C and photomask D (Figure 10). The edge of PUA elastomers fabricated using molds had minor cracks, and the edge of PUA

elastomer fabricated using photomask was soft than the body of the elastomer because of undercrosslink at the edge. As a result, the samples fabricated using a mold or a mask were also fractured earlier than they were supposed to be. Therefore, we decided to fabricate PUA elastomers in a shape of simple strip for further tensile test.

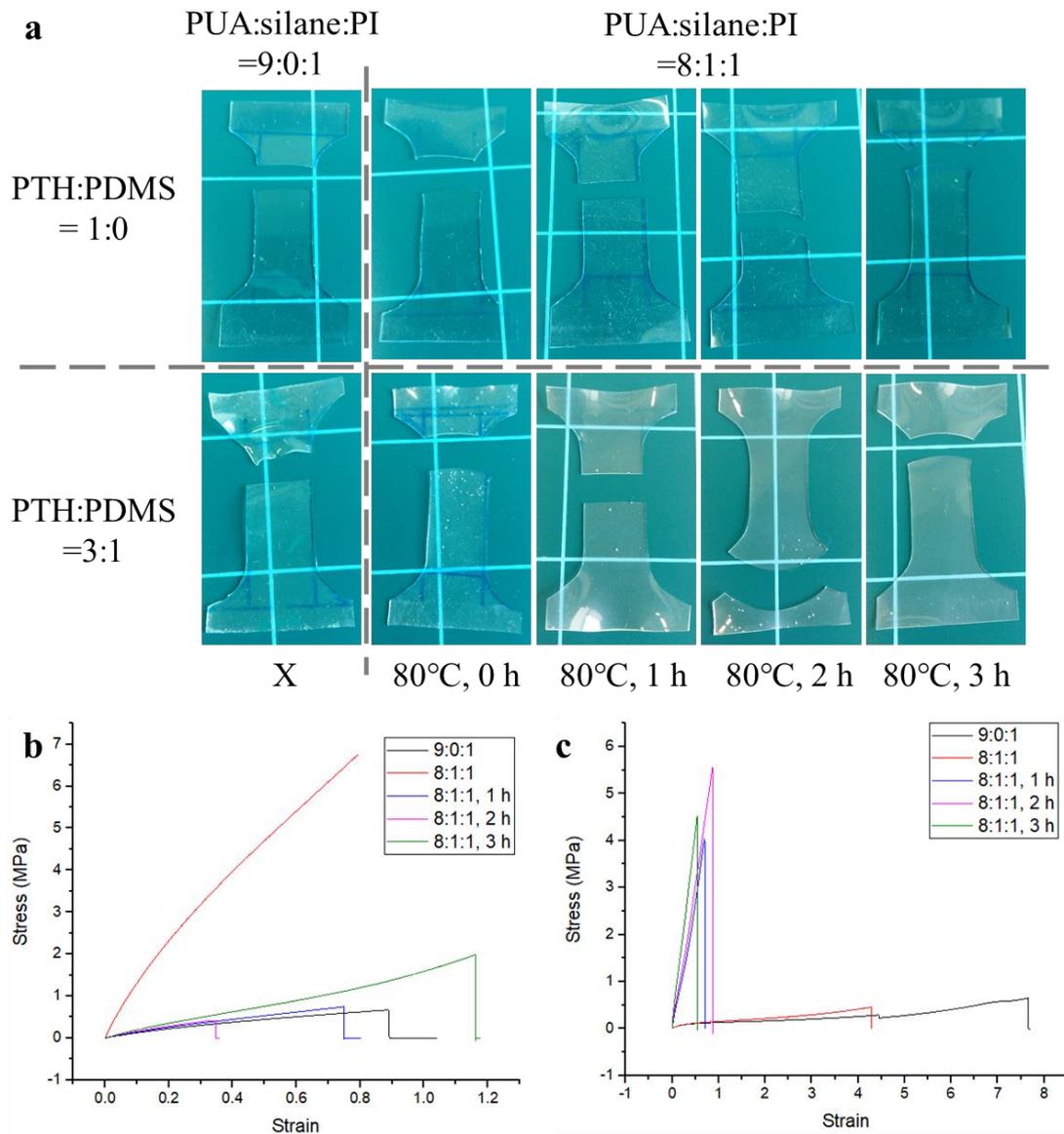


Figure 9. (a) Fractured polyurethane elastomers after tensile test. Samples in a top row were made from PUA synthesized using only PTH₂₀₀₀ as diol monomers, and samples in a bottom row were made from PUA synthesized using the mixture of PTH₂₀₀₀ and PDMS in a ratio of 3

to 1. Samples in the first column made from prepolymer mixture consists of 45 v% PUA, 5 v% Darocur 1173 (photoinitiator, PI) and 50 v% ethanol. Samples in the first column made from prepolymer mixture consists of 40 v% PUA, 5 v% Darocur 1173 (photoinitiator, PI), 5 v% 3-(trimethoxysilyl)propyl acrylate (Silane) and 50 v% ethanol. (b) Stress-strain curves from the sample made from PUA synthesized using only PTH as diol monomers. (c) Stress-strain curves from the samples made from PUA synthesized using the mixture of PTH and PDMS in a ratio of 3 to 1.

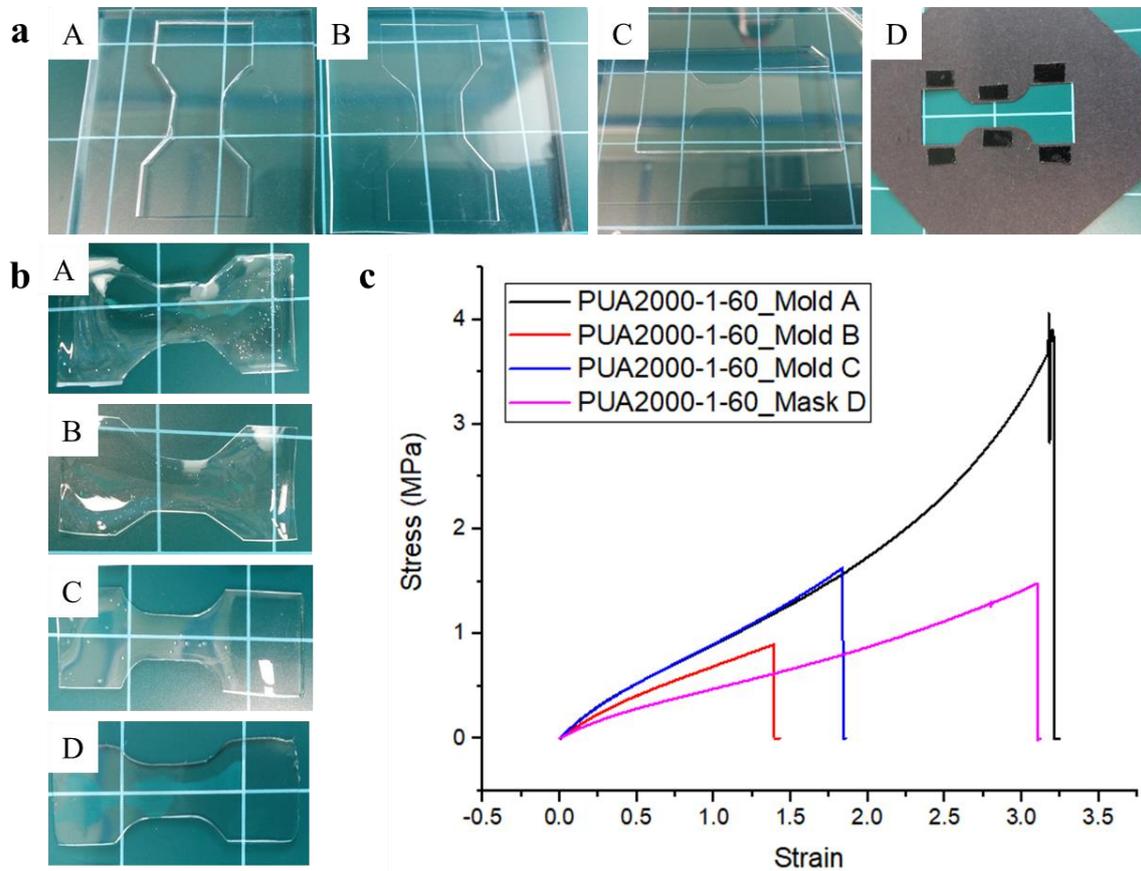


Figure 10. Dumbbell shaped PUA elastomers fabricated from PDMS molds and a photomask. (a) PDMS molds and a photomask used to fabricate PUA elastomers. Mold A, B and C have 1.4 mm, 0.4 mm and 0.4 mm depth, respectively. (b) Dumbbell shaped PUA₂₀₀₀₋₁₋₆₀ elastomers. The thickness of elastomer A,B,C and D is 1.4 mm, 0.4 mm, 0.4 mm and 0.4 mm, respectively. (c) Stress-strain curve of each elastomer made from different mold or mask.

The stress-strain curves of each PUA resin was obtained from tensile test (Figure 11 and 12). Two types of PTH was used to synthesize the PUA resin: PTH having a molecular weight of 650 g/mol (PTH₆₅₀) and PTH having a molecular weight of 2000 g/mol (PTH₂₀₀₀). PUA elastomers prepared using PUA₆₅₀ were expected to have higher modulus and lower elongation at break than PUA elastomers prepared using PUA₂₀₀₀. Since the molecular weight of PUA₆₅₀ is much lower than that of PUA₂₀₀₀, the distance between photocrosslinking sites in PUA₆₅₀ elastomers are shorter than that of PUA₂₀₀₀ and it makes higher crosslinking density in a polymer matrix. Higher crosslinking density improves modulus, ultimate tensile strength and hardness and inhibits the polymer matrix from extending since there will be less entanglement between each crosslinking site.

Instead of using PTH only to synthesize PUA, PDMS molecules were also used to synthesize PUA to add Si-O bond to the main chain. Si-O bond stretches more than carbon-carbon bond, so it makes the chain more flexible and elastic. Furthermore, 3-(trimethoxysilyl)propyl acrylate was incorporated to the photocrosslinked PUA matrix. At elevated temperature, Si-O bonds are newly formed among 3-(trimethoxysilyl)propyl acrylate. Therefore, the mechanical strength of PUA elastomer can be enhanced from the formation of new Si-O bonds by simply baking the elastomer.

In the presence of PDMS moieties in the PUA backbone, the PUA elastomers showed higher mechanical property enhancement (Table 2 and Figure 13). The result can be explained by a formation of Si-O bonds not only between 3-(trimethoxysilyl)propyl acrylate molecules themselves, but between 3-(trimethoxysilyl)propyl acrylate molecules and PDMS moieties in a backbone. When PDMS moieties are in the main chain, there are more chances for Si-O bonds to be formed than in a case of the absence of PDMS.

While both PUA₆₅₀ and PUA₂₀₀₀ having PDMS moieties in the main chain, the mechanical properties of PUA₆₅₀ were more affected by baking at elevated temperature than those of PUA₂₀₀₀. Since the molecular weight of PUA₆₅₀ is lower than that of PUA₂₀₀₀, PUA elastomer made of PUA₆₅₀ has more PDMS moieties in its polymer matrix compared to PUA elastomer made of PUA₂₀₀₀ having the same volume. Therefore, the result can be explained as a higher density of Si-O bonds in PUA elastomer made of PUA₆₅₀ than PUA₂₀₀₀ at a given volume.

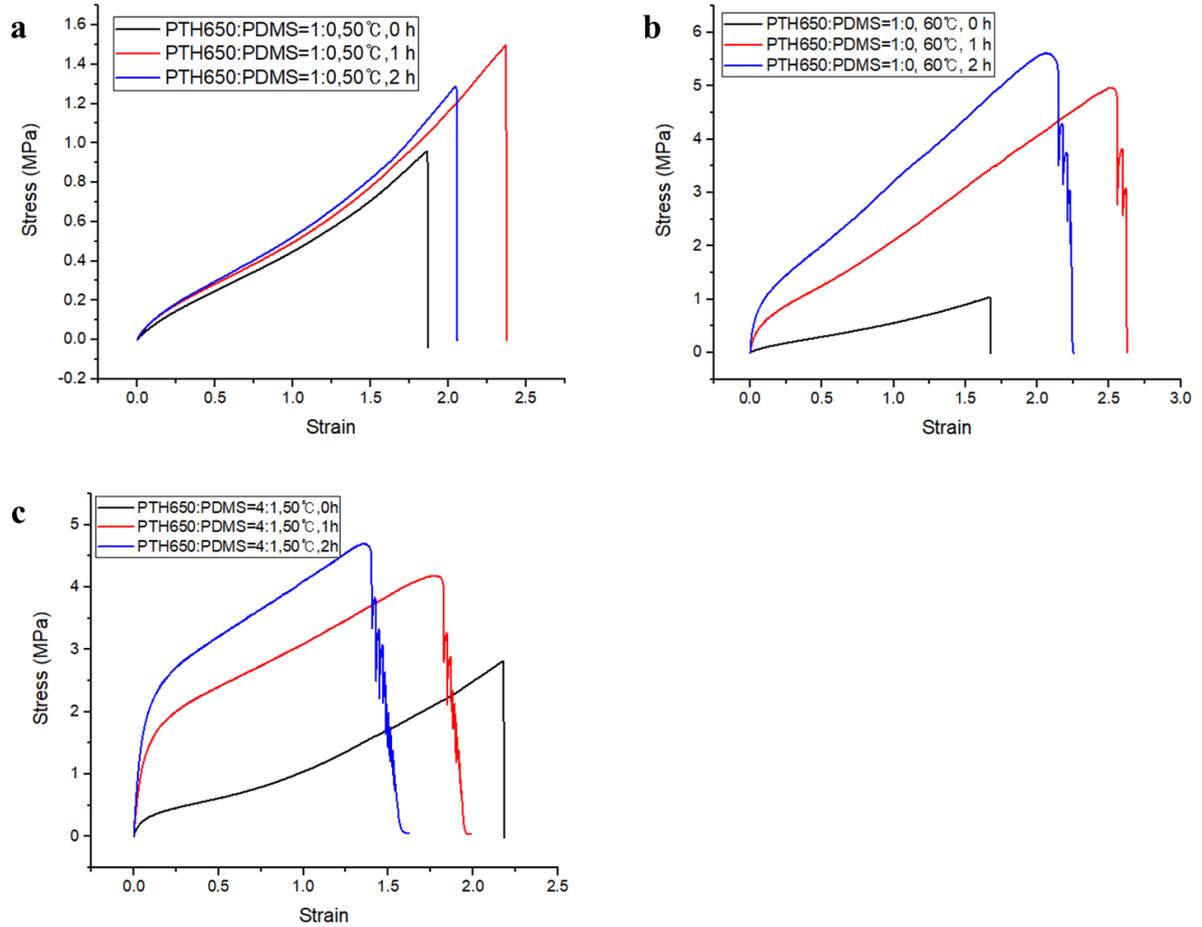


Figure 11. Stress-strain curve of (a) PUA₆₅₀₋₀₋₅₀, (b) PUA₆₅₀₋₀₋₆₀, and (c) PUA₆₅₀₋₁₋₅₀. The size of each sample is 7 mm*25 mm*0.4 mm. The elastomers were baked at 80°C for an hour or two hours to enhance their mechanical properties.

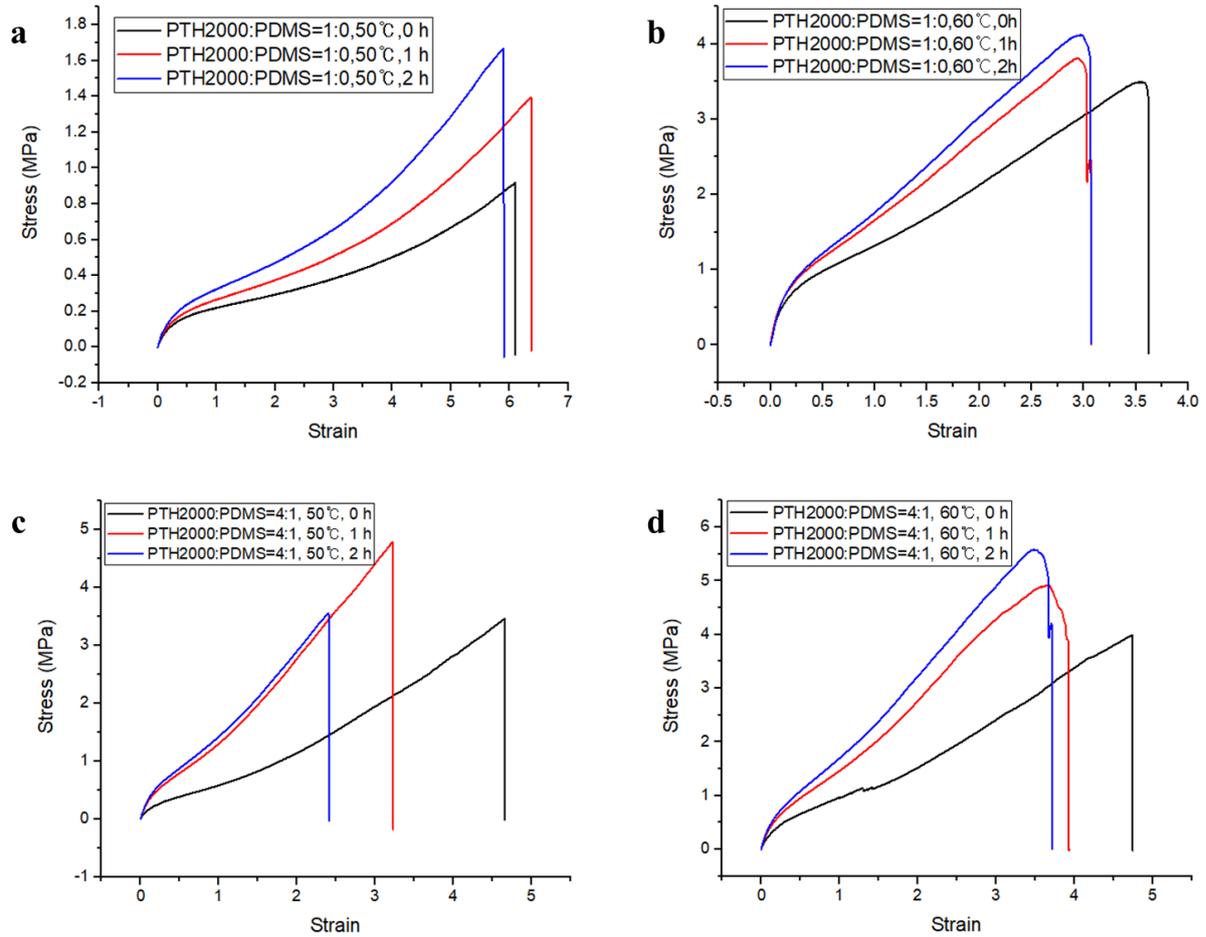


Figure 12. Stress-strain curve of (a) PUA₂₀₀₀₋₀₋₅₀, (b) PUA₂₀₀₀₋₀₋₆₀, (c) PUA₂₀₀₀₋₁₋₅₀ and (d) PUA₂₀₀₀₋₁₋₆₀. The size of each sample is 7 mm*25 mm*0.4 mm. The elastomers were baked at 80°C for an hour or two hours a given time to enhance their mechanical properties.

Table 2. Young's modulus (E) of each PUA elastomers.

Young's Modulus (MPa)	PUA	PUA	PUA	PUA	PUA	PUA	PUA
	650-0-50	650-0-60	650-1-50	2000-0-50	2000-0-60	2000-1-50	2000-1-60
0	0.61	1.80	2.10	0.54	3.38	1.19	2.01
1 h	0.77	2.95	9.39	0.61	3.90	2.38	2.88
2 h	0.79	3.38	12.87	0.73	4.00	2.65	3.23

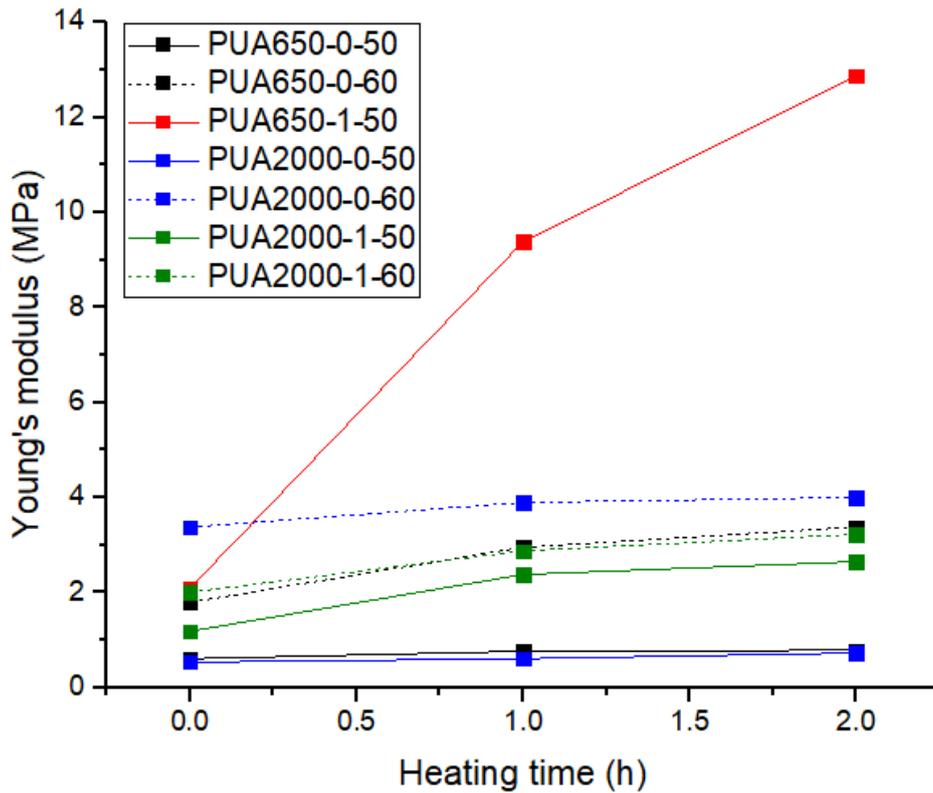


Figure 13. Young's modulus (E) of each PUA elastomers versus heating time.

3.3 Selective Modulus Enhancement of PUA Elastomers

After investigating elastomers which was enhanced its overall mechanical strength, local modulus enhancement was tested using PUA₆₅₀₋₀₋₆₀, PUA₂₀₀₀₋₀₋₆₀, PUA₆₅₀₋₁₋₆₀ and PUA₂₀₀₀₋₁₋₆₀ elastomers (Figure 14). The half of each sample was baked at 80°C for 2 hours to enhance its modulus, and then samples were stretched to observe the deformation of a spots on the surface of the samples. Unlike other elastomers, PUA₆₅₀₋₁₋₆₀ elastomer showed the biggest difference between heated and unheated area of the elastomer. While the size of spots on heated and unheated area of the other samples was rather uniform for each sample, there was a noticeable difference between the size of spots on heated and unheated area of PUA₆₅₀₋₁₋₆₀ elastomer.

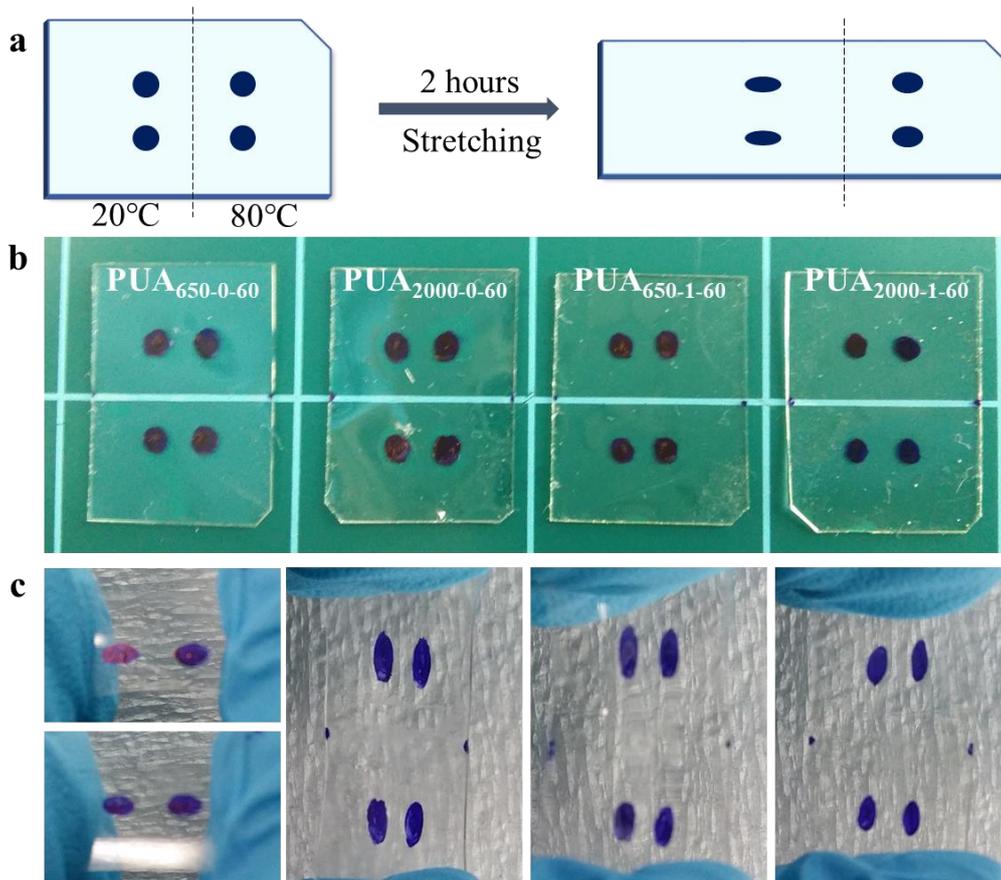


Figure 14. Local modulus enhancement test. (a) schematic view of local modulus enhancement test. (b) Half-baked elastomers fabricated from PUA₆₅₀₋₀₋₆₀, PUA₂₀₀₀₋₀₋₆₀, PUA₆₅₀₋₁₋₆₀ and PUA₂₀₀₀₋₁₋₆₀ resin. (c) Stretched elastomers after local modulus enhancement.

Since there was a clear difference between locally modulus enhanced area and the rest of the area of PUA elastomers, the selectively modulus enhanced PUA elastomers were tested again but in a smaller area of enhancement. According to the result of tensile test (Figure 11 and 12), PUA₆₅₀₋₁₋₅₀ was selected as the best suitable PUA resin among all of the resins for modulus enhancement experiment. PUA elastomers were prepared from PUA₆₅₀₋₁₋₅₀ resin, and the elastomers were selectively heated only at the center (Figure 15). After selective modulus enhancement, each film was elongated to 200% from its original length to check the amount of deformation of the spot at the center of the elastomer. As the modulus of the film was enhanced, the amount of deformation of each spot was decreased. The size of the spot in the center of the sample heated for 120 seconds was almost same even after the sample was elongated to 200% of its original size, while the spot in the first sample was largely deformed under strain.

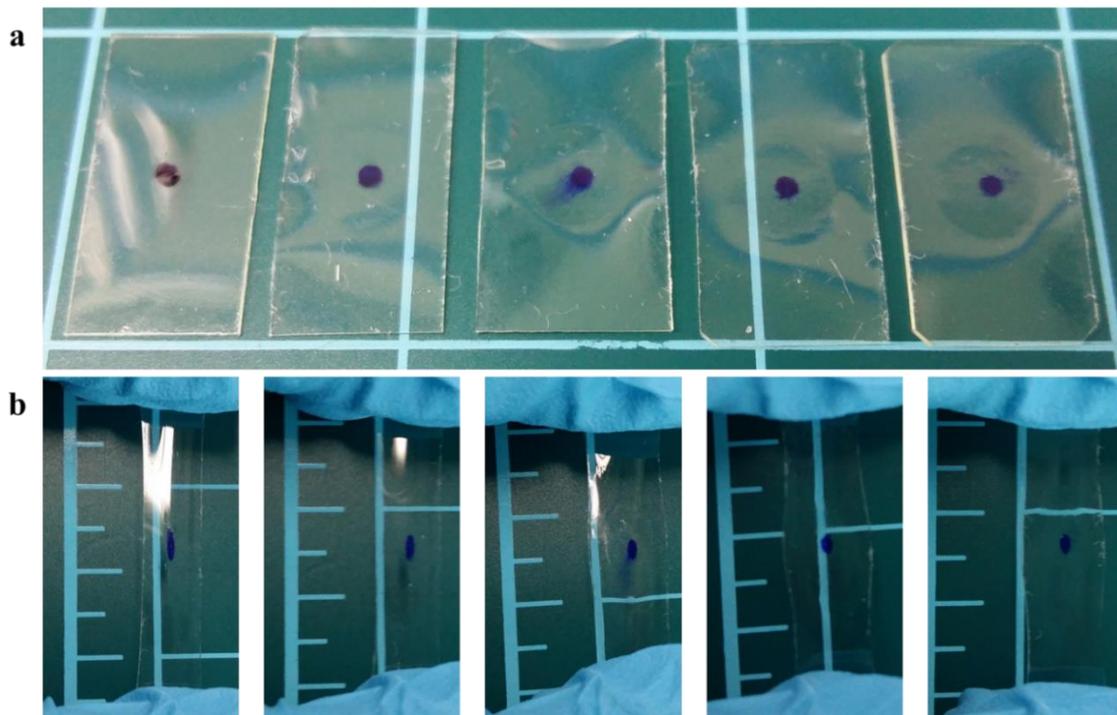


Figure 15. Selectively modulus enhanced samples and the difference of a spot size before and after modulus enhancement. (a) Selectively heated PUA₆₅₀₋₁₋₅₀ elastomer for modulus enhancement. Each of the film was selectively heated at 130°C for 0, 30, 60, 90 and 120 seconds, respectively. (b) The PUA elastomers at 200% elongation. The deformation of each spot was decreased as the modulus of the film was enhanced.

3.4 Selective Conductivity Securing

Since it is verified that modulus of PUA elastomer can be enhanced in a selective area, the selective modulus enhancement can be used to secure conductivity in a desired part of the elastomer (Figure 16). The surfaces of PUA elastomers were treated with O₂ plasma at 80 ccm for 60 seconds and coated with Pt by Pt sputtering at 20 mA for 60 seconds. When the sample is not under strain, the resistances of all samples were less than 100Ω. The resistance of PUA₆₅₀₋₀₋₅₀ under 125% strain was not measured because the value of resistance was beyond the measurable range. The resistance of PUA₆₅₀₋₀₋₆₀ under 125% strain was 10 kΩ along the heated line and 20 kΩ vertical to the heated line. The resistance of PUA₆₅₀₋₁₋₅₀ under 125% strain was not measurable along the heated line and 1.7 kΩ along the vertical line to the heated line. The selectively heated area of PUA₆₅₀₋₀₋₅₀ elastomer has low modulus even after heating as shown in Figure 13, thus the conductivity of a Pt layer on PUA₆₅₀₋₀₋₅₀ elastomer was lost when the elastomer was under strain. The conductivity of a Pt layer on PUA₆₅₀₋₀₋₆₀ elastomer was slightly remained after sample elongation in both direction, along the heated line and vertical to the heated line. The conductivity of Pt layer on PUA₆₅₀₋₁₋₅₀ elastomer was lost along the heated line, and only remained in a direction vertical to the heated line. The reason why the conductivity of Pt layer on PUA elastomers was remained is that newly formed Si-O bonds between 3-(trimethoxysilyl)propyl acrylate molecules and PDMS moieties in backbone help the elastomer to maintain its original shape under strain, and thus Pt layers were less cracked on modulus enhanced areas.

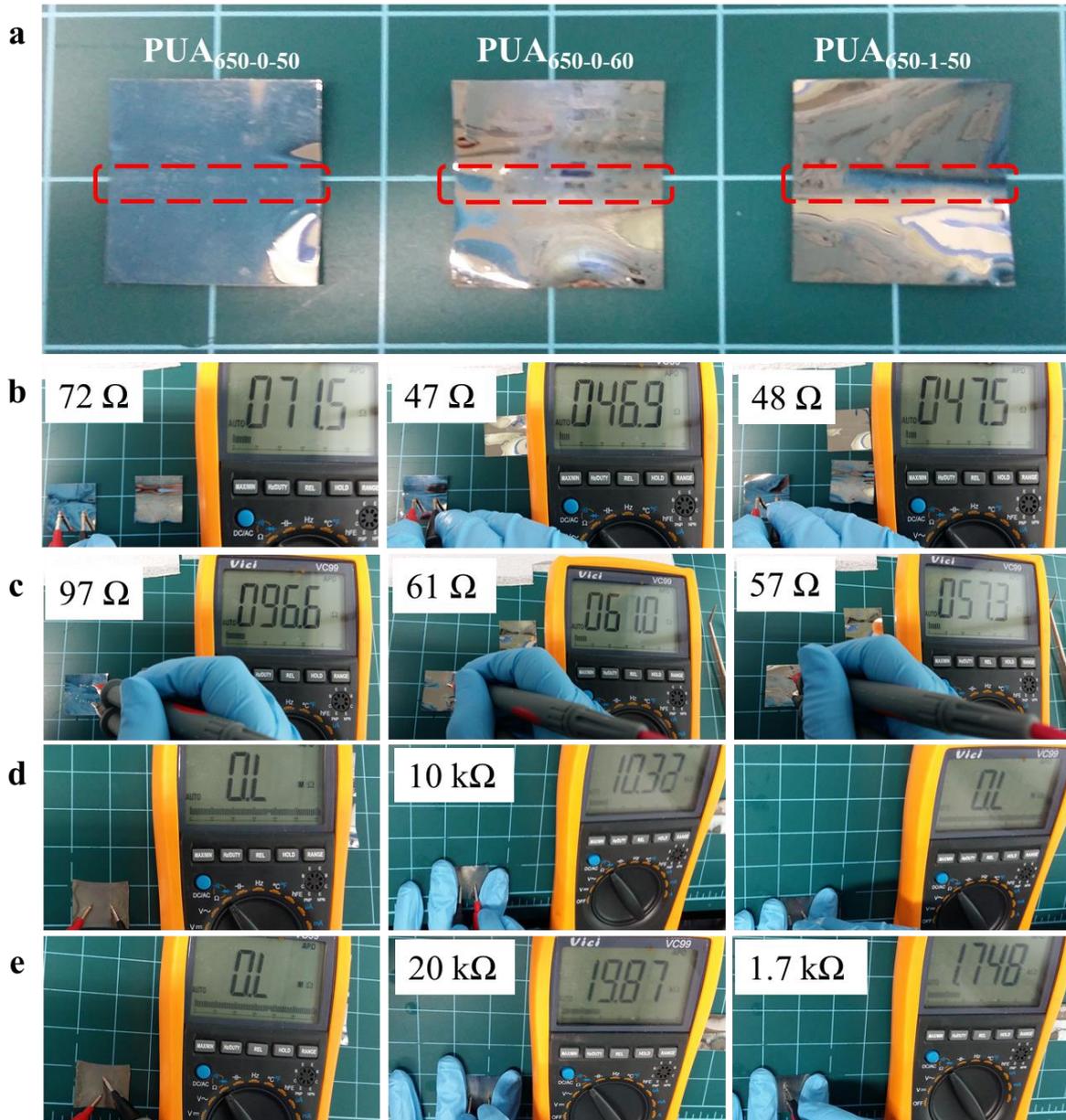


Figure 16. (a) Pt coated PUA elastomers: PUA₆₅₀₋₀₋₅₀, PUA₆₅₀₋₀₋₆₀ and PUA₆₅₀₋₁₋₅₀, respectively. Highlighted areas are heated at 80°C for 2 hours. (b) Resistance measurement vertical to the heated line before sample elongation. (c) Resistance measurement along the heated line before sample elongation. (d) Resistance measurement vertical to the heated line at 125% strain. (e) Resistance measurement along the heated line at 125% strain.

IV. CONCLUSIONS

Polyurethane acrylate resin was successfully synthesized from PTH, hydroxy terminated PDMS and IPDI. The polyurethane chains were terminated with hydroxyethyl acrylate to enable its photocuring under 365 nm UV light with the presence of Darocur 1173 as a photoinitiator. For enhancement of the elastomer's mechanical properties, 3-(trimethoxysilyl)propyl acrylate molecules were photocured together with the polyurethane resin to fabricate a uniform polymeric elastomer. The method of enhancing modulus of the PUA elastomers were very simple: heating the elastomer above 80°C only in a desired area for specified enhancement. The overall modulus enhancement was observed by measuring strain-stress curves for each polyurethane resin using Instron universal testing equipment. Selected modulus enhancement was investigated by observing deformation of a spot drawn on a surface of the elastomer and resistance change of Pt layer on the surface of the elastomer. This UV-curable polyurethane resin with selectively tunable modulus can provide a possibility for fabricating force sensor and flexible devices with a high durability.

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