Synthesis of Self-Healing Polyurethane Urea-Based Supramolecular Materials

Young Joo Kim, Pil Ho Huh, Byung Kyu Kim

Department of Polymer Science and Engineering, Pusan National University, Busan 609–735, Korea
Correspondence to: B. K. Kim (E-mail: bkkim@pnu.edu)

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ABSTRACT: Supramolecular polyurethane ureas are expected to have superior mechanical properties primarily due to the reversible, noncovalent interactions such as hydrogen bonding interactions. We synthesized polyurethane prepolymers from small molecular weight of poly(tetramethylene ether)glycol and isophorone diisocyanates, which were end capped with propylamine to synthesize polyurethane ureas with high contents of urea and urethane groups for hydrogen-bonding formations to facilitate self-healing. The effects of polyurethane urea molecular weight ($3000 \leq M_n \leq 9000$), crosslinking, and cutting direction were studied in terms of thermal, mechanical, and morphological properties with an emphasis on the self-healing efficiency. It was found that the thermal self-healability was more pronounced as the molecular weight of polyurethane urea decreased, showing a maximum of more than 96% with 3000 M_n when the sample was cut along the stretch direction. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. **2015**, *53*, 468–474

KEYWORDS: films; hydrogen bonding; linear; polyurethanes; polyurethane urea; self-healing; supramolecular; supramolecular structures

INTRODUCTION Polyurethanes (PUs) find use in a variety of industrial applications including coatings, adhesives, sealants, elastomers, primer, sporting goods, medical devices, textile finish, and various foam products.[1–5] They are synthesized by a simple polyaddition reaction of polyol and isocyanate to form either hydroxyl- or isocyanate-terminated prepolymers. When the isocyanate-terminated prepolymers are extended by diol, all the different monomer units are covalently bonded by urethane groups and the products are simply called polyurethanes. On the other hand, when the chain extensions are made by amines, urea groups are formed in addition to the urethane groups existing in the prepolymers, and the products are often called polyurethane ureas although they are commonly called polyurethanes. The amine-extended or amine-terminated PUs generally show superior physical properties when compared with the diol-extended ones because of the strong cohesion of urea groups over the urethane groups via the hydrogen bondings.[6]

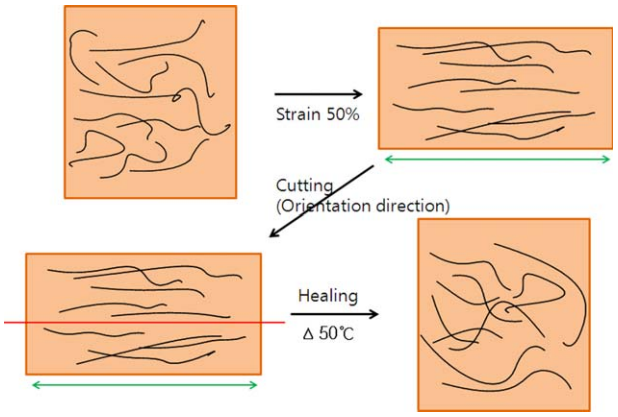
The lifetimes of polymers can be extended if they have ability to repair themselves after sustaining damage in many applications.[7,8] The so-called self-healing polymers are at the forefront of polymer research, and significant contributions have become available with regard to the thermodynamic requirements, primary interactions, encapsulation, remote control, and shape-memory effects.[9] With self-healability, the lifetimes of polymers can be extended as they have an ability to repair themselves after sustaining damage in many applications.[7,8] When the polymers are fractured, their properties can be regained either autonomically[10,11] or in response to an external stimulus such as heat[12] or pressure.[13]

The self-healing of PUs has been a hot issue in recent years.[7,8,10–22] The near-infrared absorption of graphene has been incorporated into the PUs for self-healing nanocomposites, where the chemically modified graphene gave dual effects of reinforcing filler and light absorption medium.[4,15]

A protective PU self-heating coating that simultaneously inhibits corrosion from occurring on the protected substrate has also been reported.[16]

Wang et al. reported polydimethylsiloxane–PU crosslinked networks capable of repairing mechanical damage on UV exposure, where copper chloride catalyst induced the network reformation by the formation of Cu—O coordination complexes and covalent Si—O—Si hydrolysis.[17–19]

Recently, thermoresponsive self-healing PUs based on the Diels–Alder reaction between furan and maleimide moieties were reported, where the shape-memory effect was used to autonomously close the crack.[20,21]



SCHEME 1 Healing mechanism for the oriented films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polyurethane microcapsules containing water-borne PU paint as a core material for self-repairing protection coatings were manufactured via interfacial polymerization of diol–diisocyanate prepolymer and 1,4-butanediol as a chain extender in an emulsion solution.[22]

Healable polymers include encapsulated monomers and polymerization catalysts[11,14] and latent functionalities which are able to participate in thermally reversible, covalent bond-forming reactions.[12,23,24] It has been known that noncovalent interactions, specifically hydrogen bonds, can be used to affect healing within a supramolecular polymer blend.[12,25] If the commodity polymers are subject to the self-healing by molecular design, newer applications are expected for value-aided products.[4,26–30]

In this work, we synthesized PU from relatively small molecular weight of poly(tetramethylene ether)glycol (PTMG300) and molar excess of isophorone diisocyanates (IPDIs), which were subsequently end capped with propylamine to synthesize polyurethane ureas with various molecular weights in the range of 3000–9000. High contents of urethane groups and urea groups were introduced by using small molecular weights of polyol and PU, respectively, to provide the superstructure structures with endowed self-healing effects via the hydrogen bondings.[6] In addition, films were cut parallel and perpendicular to the stretch direction as well as in random direction to examine the effects of chain orientation and bond type on self-healing. Scheme 1 shows the healing mechanism for the oriented film corresponding to the parallel direction cutting.

TABLE 1 Recipe of PU Synthesis, T_g, and Gel Contents (GC) for the Films

	Polyurethane (g)					
Series	PTMG300	IPDI	Propylamine	APTES (g)	T_g (°C)	GC (%)
LPU30	12.92	15.90	1.18	–	16.85	0
LPU50	13.58	15.71	0.71	–	20.12	0
LPU70	13.86	15.63	0.51	–	23.01	0
LPU90	14.02	15.58	0.31	–	25.56	0
CPU70	13.13	14.91	–	1.90	40.28	97.8

Numbers following the PU correspond to the M_n of the polymers: LPU30 = 3000 M_n. Total solid: 30 g.

EXPERIMENTAL

Raw Materials

Poly(tetramethylene ether)glycol (PTMG diol, $M_n = 300$; Sigma-Aldrich) was dried and degassed at 80 °C under vacuum for 3 h before use. Isophorone diisocyanate (IPDI; Aldrich) was dried over 4 Å molecular sieves before use. Propylamine, 3-aminopropyltriethoxysilane (APTES), dibutyltindilaurate (Aldrich), and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU; Aldrich) were used as received. Dimethylformaldehyde was used as solvent.

Preparation of Linear Polyurethane and Crosslinked Polyurethane

The recipe to synthesize the linear PU (LPU) is shown in Table 1 along with the reaction scheme in Figure 1(a). PTMG diol having molecular weight of 300 g/mol was placed in a 500-mL four-necked flask with a mechanical stirrer, thermometer, and condenser with a drying tube. Molar excess of

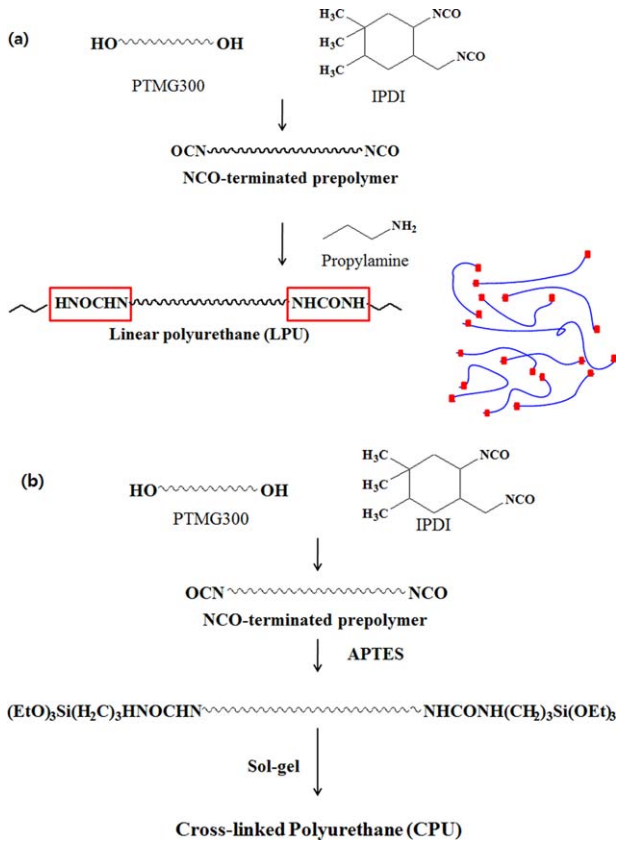


FIGURE 1 Overall reaction scheme to prepare (a) LPU and (b) CPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

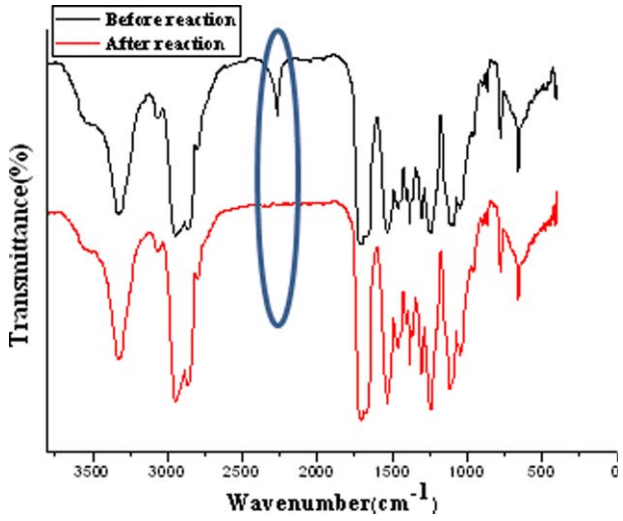


FIGURE 2 Typical FTIR spectra of the PU before and after propylamine capping (LPU70). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

IPDI was added, and the urethane-forming reaction was carried out in a constant temperature oil bath at 70 °C. The NCO-terminated LPU was end capped with propylamine at 40 °C to obtain LPU of molecular weight of about 3000, 5000, 7000, and 9000 determined by the isocyanate index ([NCO]/[OH]). The progress of reaction has been monitored by Fourier transform infrared (FTIR) measurements (Fig. 2), where the absorption peak of NCO at 2270 cm^{-1} is completely disappeared on capping with propylamine. Then, the amine-capped LPU was cooled down to room temperature and stabilized by steadily stirring during the next 1 h.

On the other hand, the crosslinked polyurethane (CPU) was prepared by capping the isocyanate-terminated prepolymers with APTES, followed by the sol–gel reactions [Table 1 and Fig. 1(b)]. After checking the absorption peak of NCO at 2270 cm^{-1}, the APTES-capped PU was cooled down to room temperature. To hydrolyze the ethoxy groups of APTES, a 1:1 mixture of distilled water and ethanol (0.2%) was added to the prepolymer solution with DBU catalyst. Subsequently, the prepolymer solutions were cast on a Teflon plate and dried to form films. The condensation reactions between the silanol groups of APTES occurred during the drying in an oven at 80 °C to form crosslinks between the PUs.

Measurements

End-capping reactions of the NCO termini with propylamine and APTES (to form LPU and CPU) and sol–gel reactions between APTES were confirmed by FTIR spectra. Samples for infrared analysis were prepared by drying the solution directly on a KBR pellet. For this, part of the reaction mixture was taken every 0.5 h for IR analysis.

The tensile properties of cast film were measured at room temperature with a Universal Testing Machine at a crosshead speed of 500 mm/min using specimens prepared according to ASTM D-1822. Thermal analyses were carried out with differential scanning calorimetry (DSC; Seiko DSC 220) over −60 to 100 °C at a heating rate of 10 °C/min. To obtain the fractured surfaces of the oriented films, films were stretched up to 50% at the same extension rate and cut along the stretch direction using a mounted razor. On the other hand, random cut was made using the as-cast film. For both cases, the thermally induced self-healing was done in an electric oven at 50 °C for 60 min after the fractured surfaces were put together.

To measure the gel content (GC), known weight (W_0) of sample measuring 10 mm × 10 mm × 0.5 mm was put into 20 mL THF for 24 h to completely remove the uncrosslinked constituents. The samples were then dried in oven at 70 °C and weighed (W_t). GC was then calculated using the following equation:

$$\%\text{Gel} = \frac{W_t}{W_0} \times 100.$$

The thermally induced self-healing of the scratched film surface was monitored with an optical microscope (Eclipse LV100; Nikon) equipped with an Artcam-300MI-DS digital camera.

The healed specimens were subjected to tensile test as above. Healing efficiency (HE) is defined using the modulus of toughness[7,24] as follows:

$$\text{Healing efficiency (HE)} = \frac{\text{toughness}_{\text{healed}}}{\text{toughness}_{\text{original}}} \times 100\ (\%).$$

The modulus of toughness is a measure of the strain energy required to break the material and corresponds to the area under the stress–strain curve.[7,24,31–33]

RESULTS AND DISCUSSION

FTIR Spectra of APTES End Capping

The FTIR measurements (Fig. 2) show that the characteristic NCO peak (2270 cm^{-1}) has completely disappeared on

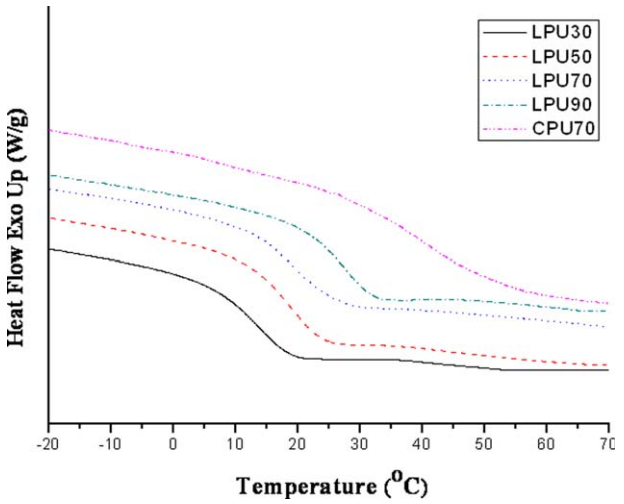


FIGURE 3 DSC thermograms of the LPU and CPU cast films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

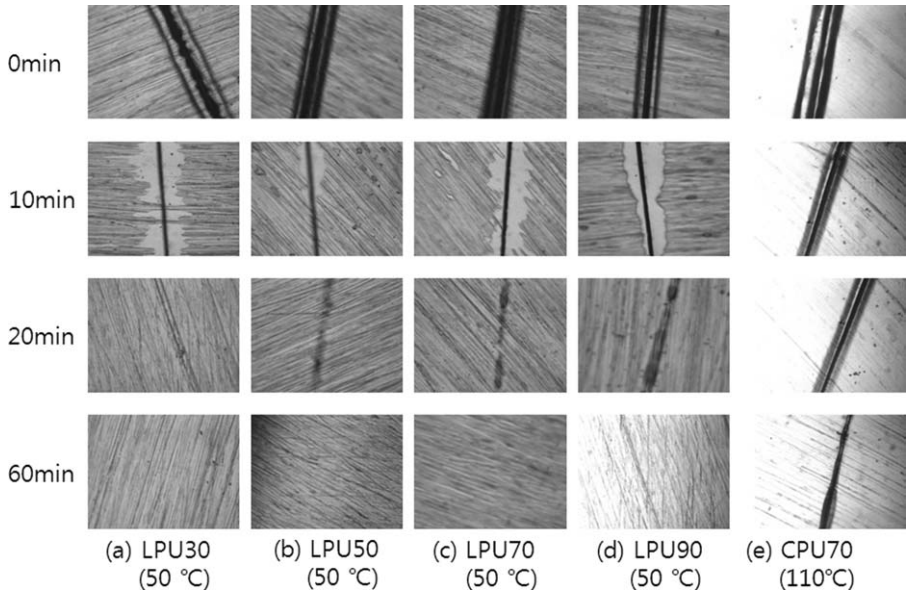


FIGURE 4 Optical microscope follow-ups of the self-healing at 50 °C and for 60 min.

capping the NCO terminal of PU prepolymer with NH_2 groups of propylamine. This confirms the formation of polyurethane ureas.

Thermal Analysis

Figure 3 shows that the glass transition temperature (T_g) of the cast film gradually increases with increasing molecular weight of the LPU in accordance with the Flory-Fox equation:[34]

$$T_g = A - \frac{B}{M_n},$$

where A and B are constants. The linear least-square analysis of the DSC data gave $A = 302$ (K) and $B = 36{,}970$ (K mol/g). The crosslinked PU (CPU70) carrying the molecular weight between the crosslinks (M_c) of 7000 shows much higher T_g (40.25 °C) than the corresponding linear PU (LPU70; 23.01 °C).

Gel Contents

The GC of CPU70 was more than 97.8%, indicating that the CPU is almost completely crosslinked. On the other hand, the GCs were essentially zero for the all LPUs (Table 1).

Optical Microscopy

Figure 4(a–d) shows that all the films cast from LPUs (LPU30, LPU50, LPU70, and LPU90) are thermally healed by direct heating at 50 °C, and healing is completed in 60 min. A typical photograph showing the self-healing is shown in Figure 5 for LPU70. The cut surface (left) was completely healed (right) on exposure to the direct heat at 50 °C for 60 min.

On the contrary, the crosslinked PU (CPU70) was not healed at 50 °C, temperature higher than the T_g (40.28 °C). The CPU was slowly and partially healed at 110 °C [Fig. 4(e)], implying that diffusion of polymer chains through the

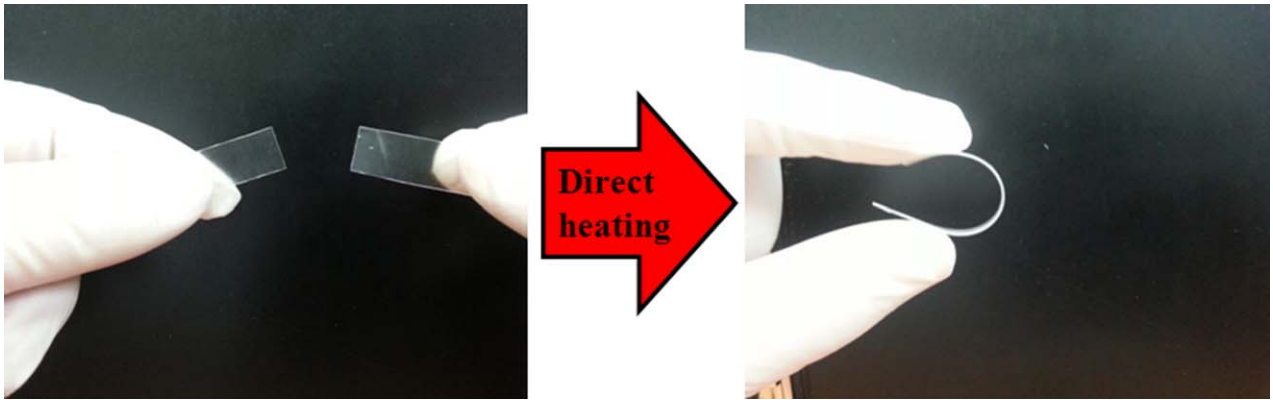


FIGURE 5 Typical digital photograph of the self-healing (LPU70, self-healing at 50 °C for and 60 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

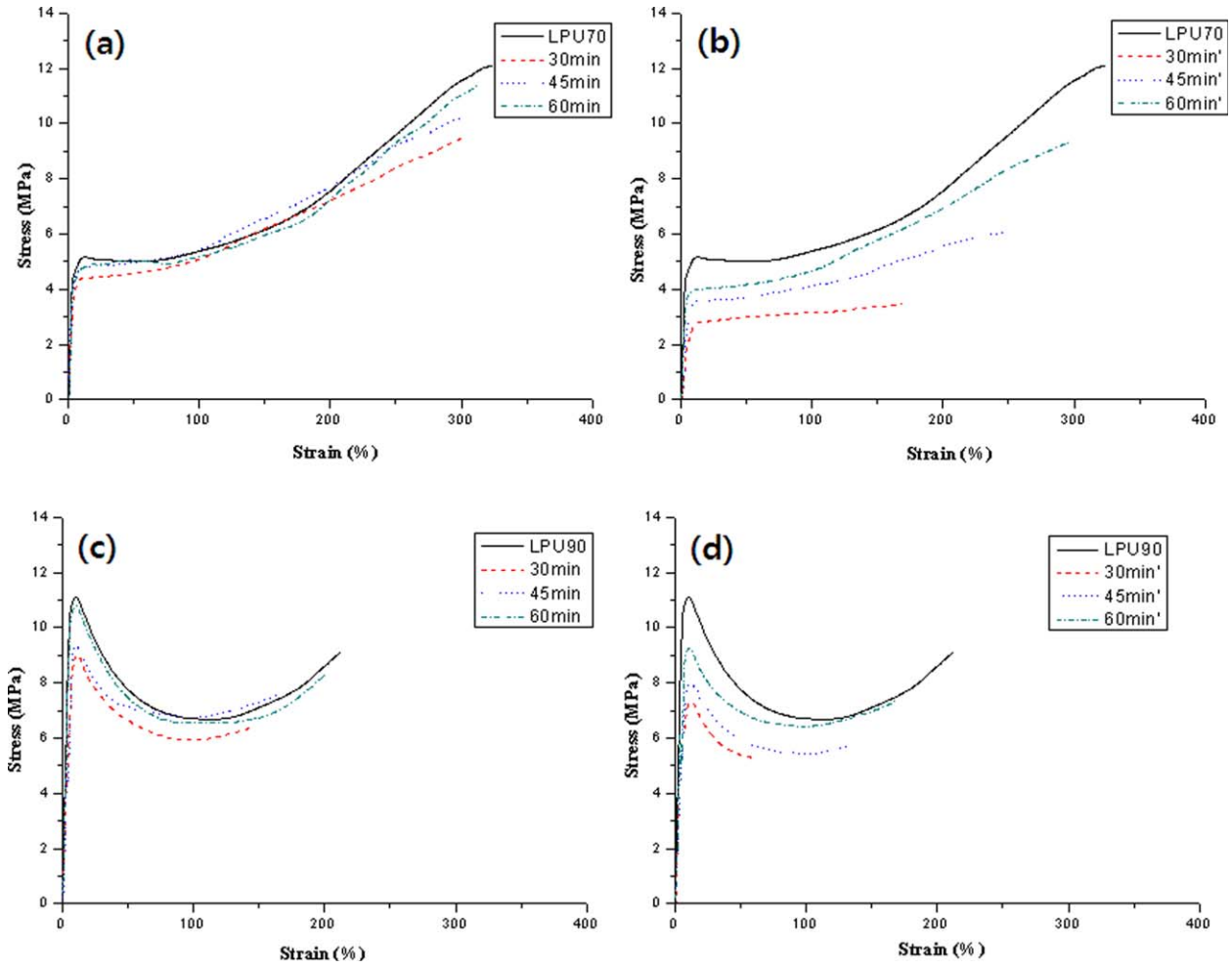


FIGURE 6 Stress–strain behavior follow-ups of the self-healing at 50 °C and for 60 min: (a and b) LPU70; (c and d) LPU90 [(a) and (c) for parallel cut; (b) and (d) for random cut]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslinked mass with little free volume is extremely slow even at high enough temperature.

Tensile and Healing Tests

Typical tensile and healing behaviors of the LPUs at room temperature are shown in Figure 6 for LPU70 and LPU90, and the details are summarized in Table 2 for all the LPUs. Several things were obvious from the tests. With increasing M_n of PU, initial modulus, break strength, and elongation at break increased. Exception was found for LPU90, where elongation at break rather decreased. This is due to the fact that LPU90 is in the glassy state when compared with the rubbery state for the other LPUs.

On the other hand, the HE (recovery of the original stress–strain behavior; Table 2) decreased as the M_n of the polymer increased due to the decreased content of urea groups and decreased rate of interchain diffusion. Urea groups provide the materials with hydrogen bondings where the diffusion rate decreases with increasing molecular weight due to the increased viscosity.

Regarding the cutting direction, parallel cutting, namely, cutting along the stretch direction shows much great HE over the random cutting. This implies that parallel cutting cuts minimum number of primary bondings, and hence the healing is largely facilitated by the secondary bonds, namely, hydrogen bonds. Parallel cutting implies that the specimen is cut along the stretch direction. As the polymer chains are preferably oriented along the stretch direction, interchain bondings are mostly secondary bonds such as hydrogen bond and van der Waals forces rather than the covalent bonds. This makes the self-healing of parallel cutting much more feasible than the random and perpendicular cuttings. The effect of cut direction is more pronounced with large M_n polymers. For example, for the first 30 min of heating, HEs of LPU30 were 88.2% (parallel cutting) and 52.8% (random cutting), whereas HEs of LPU90 were 58.3% (parallel cutting) and 20.30% (random cutting). The reasons are as follows: large M_n polymers have fewer chain ends and are more vulnerable to primary bond cleavage. This is critical to the random cutting but much less for parallel cutting as chain orientations are more feasible and relaxation is slow for large M_n polymers. The secondary bond effects are more pronounced with the low M_n polymers. It is mentioned that healing test was not done for CPU as fractured surface was

TABLE 2 Tensile Properties and Healing Efficiency (HE) of Parallel Cut Films (a, c, e, g, and i) and Random Cut Films (b, d, f, and h) for Various Healing Times

	E (MPa)	σ_b (MPa)	ε_b (%)	HE (%)		E (MPa)	σ_b (MPa)	ε_b (%)	HE (%)
(a)					(b)				
LPU30	54.26	1.57	104.87	–	LPU30	54.26	1.57	104.87	–
30 min	53.28 ± 1.31	1.34 ± 0.21	100.99 ± 6.86	88.20 ± 4.56	30 min′	49.56 ± 2.20	1.13 ± 0.15	69.45 ± 6.25	52.81 ± 4.56
45 min	53.86 ± 1.01	1.36 ± 0.24	102.06 ± 5.71	94.94 ± 4.24	45 min′	52.52 ± 1.21	1.23 ± 0.09	71.86 ± 4.25	68.18 ± 5.04
60 min	53.90 ± 1.25	1.50 ± 0.25	103.72 ± 5.83	96.63 ± 5.72	60 min′	52.60 ± 1.75	1.48 ± 0.12	95.97 ± 5.25	88.76 ± 5.21
©					(d)				
LPU50	68.71	4.60	268.29	–	LPU50	68.71	4.60	268.29	–
30 min	65.28 ± 1.25 30.63 ± 4.35	4.23 ± 0.35	227.92 ± 7.25	82.22 ± 3.15	30 min′	48.71 ± 6.21	2.20 ± 0.35	194.34 ± 9.52	
45 min	65.98 ± 1.46 55.58 ± 4.68	4.98 ± 0.40	234.71 ± 7.23	87.21 ± 2.15	45 min′	52.63 ± 3.38	3.72 ± 0.28	213.18 ± 9.86	
60 min	67.72 ± 1.85 74.14 ± 5.35	4.37 ± 0.38	257.61 ± 6.35	90.37 ± 1.53	60 min′	54.26 ± 3.28	4.43 ± 0.28	241.5 ± 8.56	
(e)					(f)				
LPU70	110.68	12.07	324.56	–	LPU70	110.68	12.07	324.56	–
30 min	108.83 ± 1.02	9.45 ± 0.96	300.12 ± 6.35	80.01 ± 4.56	30 min′	92.63 ± 2.45	3.48 ± 1.31	169.39 ± 10.86	22.60 ± 3.56
45 min	108.72 ± 1.86	10.30 ± 0.85	304.52 ± 6.32	83.30 ± 4.86	45 min′	98.63 ± 3.11	6.10 ± 2.11	249.79 ± 11.85	47.55 ± 4.25
60 min	109.63 ± 1.10	11.38 ± 0.75	312.58 ± 5.32	88.10 ± 3.98	60 min′	99.87 ± 3.25	9.37 ± 1.31	297.72 ± 8.52	69.60 ± 3.65
(g)					(h)				
LPU90	228.37	9.07	211.21	–	LPU90	228.37	9.07	211.21	–
30 min	224.35 ± 0.56	6.39 ± 1.02	145.63 ± 8.56	58.37 ± 2.31	30 min′	170.54 ± 5.23	5.27 ± 1.23	60.45 ± 9.86	20.30 ± 3.69
45 min	225.68 ± 1.02	7.60 ± 0.83	165.99 ± 8.25	72.97 ± 3.52	45 min′	182.54 ± 2.32	5.74 ± 1.31	134.93 ± 10.56	42.30 ± 2.65
60 min	227.98 ± 0.86	8.26 ± 0.56	199.83 ± 5.20	84.98 ± 2.12	60 min′	188.42 ± 3.53	7.41 ± 1.00	171.08 ± 6.32	67.95 ± 3.87
(i)									
CPU70	732.63		25.89		62.96				–
30 min	–		–		–				–
45 min	–		–		–				–
60 min	–		–		–				–

not bonded as was seen from the optical microscope [Fig. 4(e)].

CONCLUSIONS

Supramolecular PU synthesized from PTMG300 and IPDI and terminated by propylamine formed the second-order couplings via the hydrogen bondings between the urethane groups and urea groups showing HE more than 96%.

The self-HE increased as the molecular weight of polyurethane urea decreased due to the increased urea group density and increased polymer chain mobility. Among the two types of cutting directions, parallel cutting to the stretch direction showed much higher self-HE implying that the minimum number of primary bonds is cut.

On the other hand, the T_g and mechanical properties of the polyurethane ureas increased with the increase of molecular weight in rubbery state. The self-healability was insufficient for the crosslinked polyurethane urea as the diffusion of polymer chains through the crosslinked networks is extremely slow.

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