

Abstract

Shape memory polyurethane (SMPU) is a material that can temporarily maintain a specific shape or return to its original shape under external stimuli such as heat, light, electricity, and pH. The SMPU is widely used in drug delivery, sensors, machinery, and more. In this study, we aim to observe the changes in properties by altering isocyanate base material in synthesizing SMPU. We seek to understand how the structure of Modified MDI affects the hard segment stack that forms SMPU, and how it affects the performance of SMPU. To achieve this, we measure thermal behavior, flexibility, shape recovery ability, and temporary fixity. Based on these analyses, we find high performance with the best shape memory capability with the most suitable ingredient composition.

Synthesis

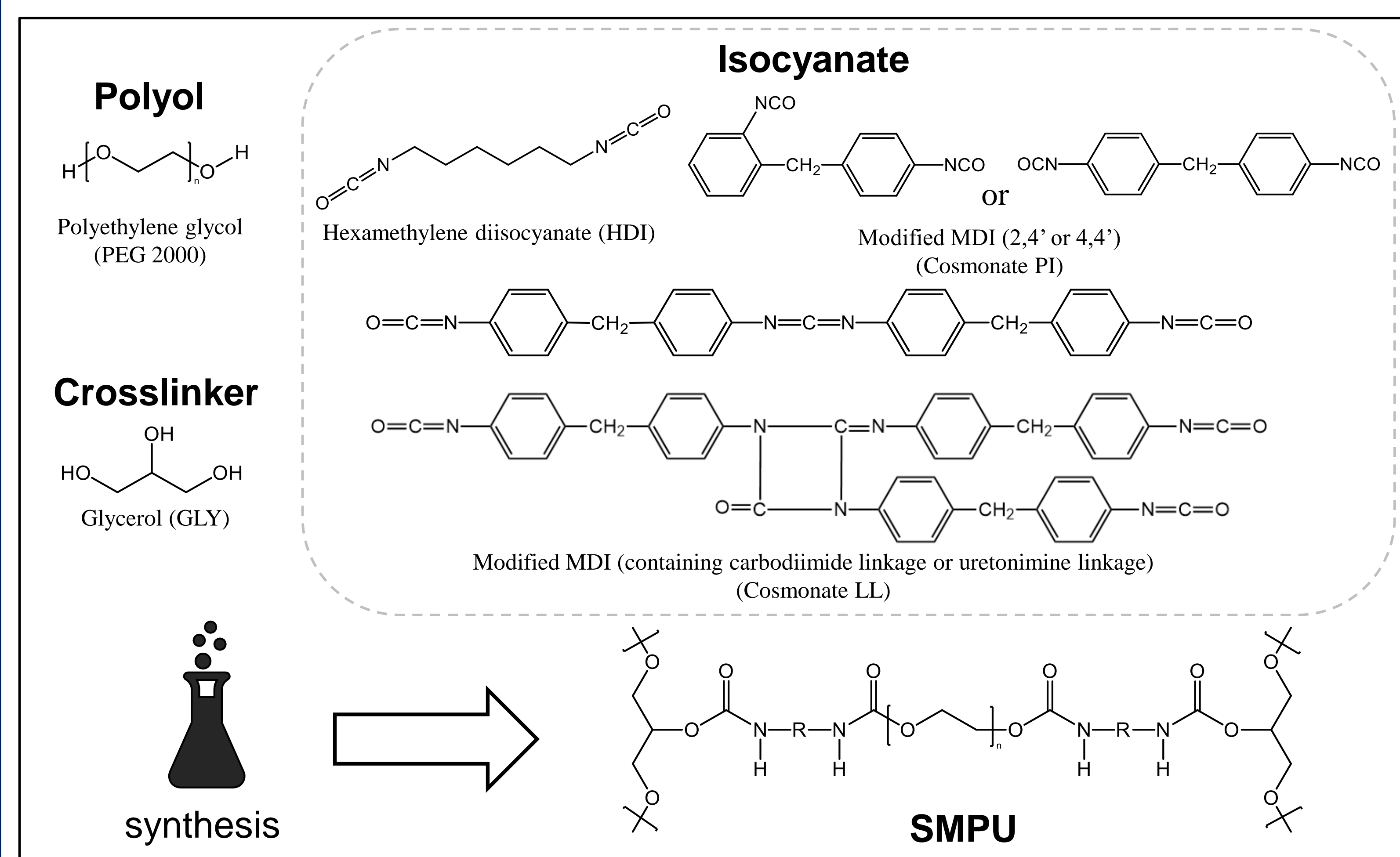


Figure 1. Chemical structure of materials and resulting polymer.

Table 1. Naming of SMPUs based on HDI and Cosmonate LL content.

Isocyanate content ratio	Cosmonate LL	Sample Name					
		HDI	LL10	LL20	LL30	LL40	LL50
		0.0	0.1	0.2	0.3	0.4	0.5
	HDI	1.0	0.9	0.8	0.7	0.6	0.5

Table 2. Naming of SMPUs based on HDI and Cosmonate PI content.

Isocyanate content ratio	Cosmonate PI	Sample Name					
		HDI	PI20	PI40	PI60	PI80	PI100
		0.0	0.2	0.4	0.6	0.8	1.0
	HDI	1.0	0.8	0.6	0.4	0.2	0.0

- Three types of isocyanate (HDI, Cosmonate LL, Cosmonate PI) were used.
- GLY contains three OH groups; hence, it can make branches and networks.
- Cosmonate LL (Kumho Mitsui Chemicals) MDI with carbodiimide bond and MDI with uretonimine bond.
- Cosmonate PI (Kumho Mitsui Chemicals) contains more than 50 area% of 2,4'-MDI, which has an ortho structure.

Principle of SMPU

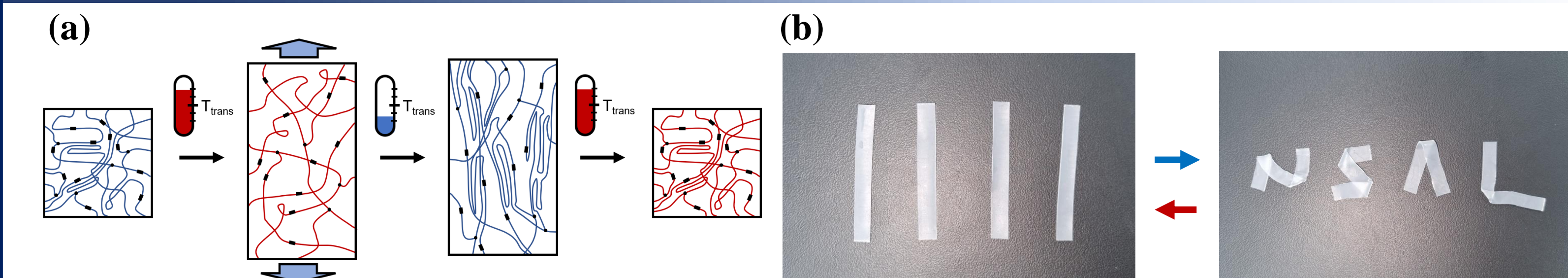


Figure 2. (a) Schematic diagram demonstrating the shape memory behavior of a SMPU specimen. (b) Photographic images displaying SMPUs reciprocating their original shapes and temporarily deformed shapes via heat.

FTIR spectroscopy

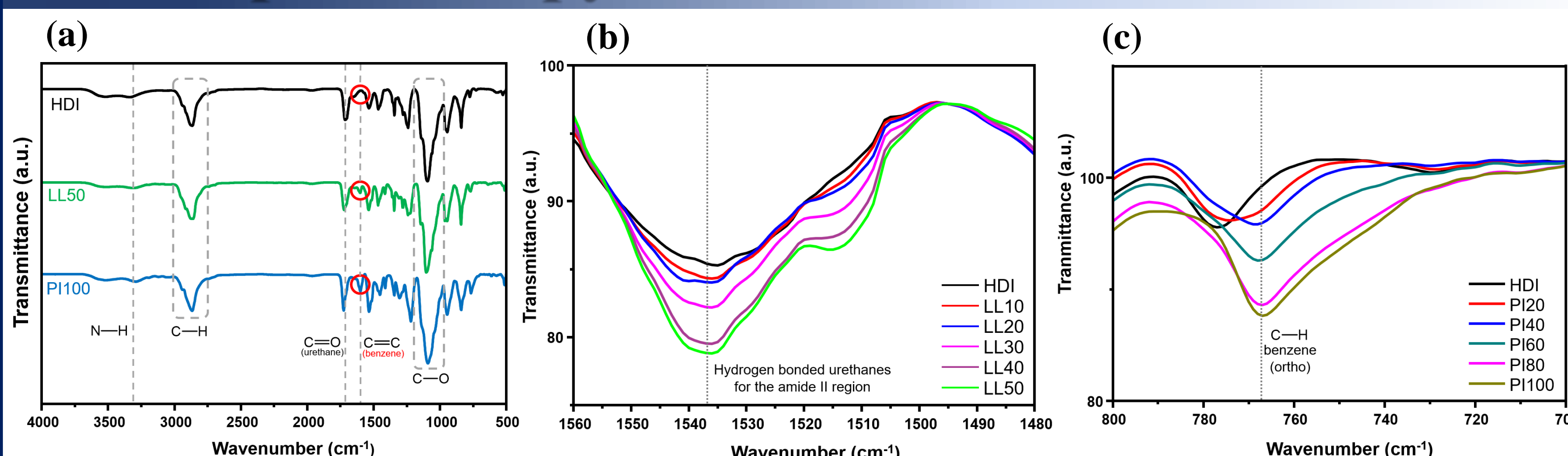


Figure 3. (a) FTIR transmittance spectra of SMPUs synthesized with different isocyanates; HDI, MDI containing carbodiimide linkage and HDI mixture, MDI (2,4' or 4,4'). (b) FTIR transmittance spectra of SMPU samples as a function Cosmonate LL content. (c) FTIR transmittance spectra of SMPU samples as a function Cosmonate PI content.

Results & Discussion

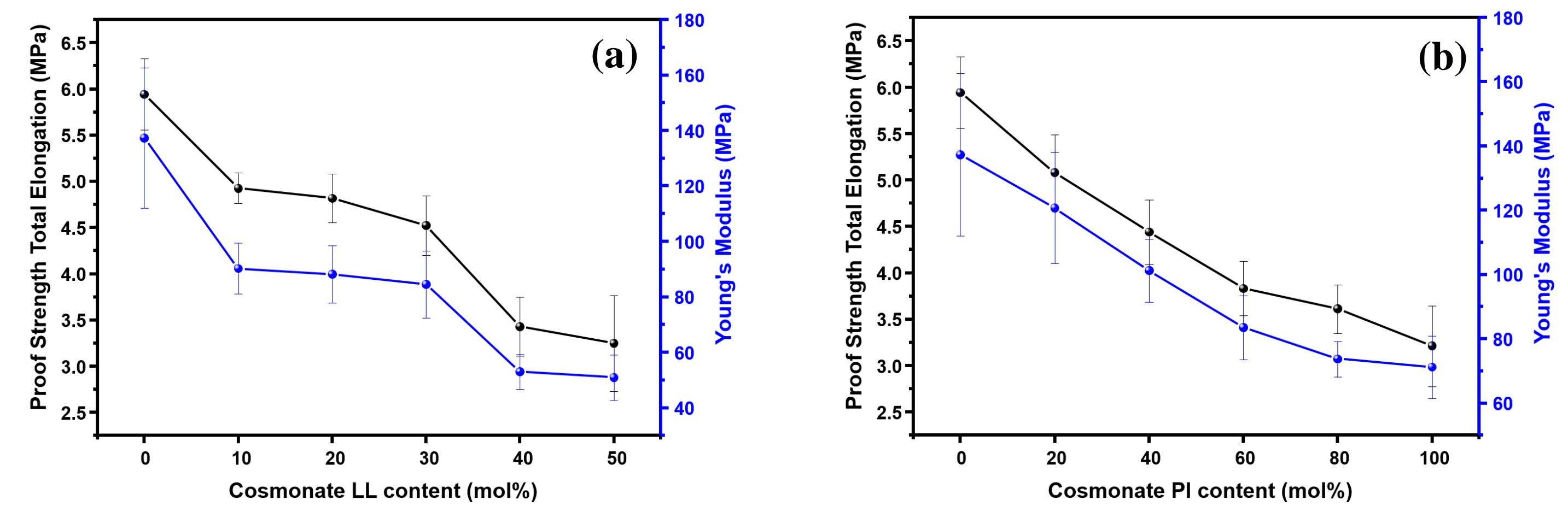


Figure 4. (a) Proof Strength Total Elongation and Young's Modulus of the SMPU samples as a function of Cosmonate LL content. (b) Proof Strength Total Elongation and Young's Modulus of the SMPU samples as a function of Cosmonate PI content.

- The test was conducted with UTM.
- As the content of MDI containing uretonimine linkage in SMPU increases, proof strength total elongation and Young's modulus decrease.
- These results are attributed to the uretonimine linkage at the center which reduces the microphase separation of the elastomer, resulting in increased elasticity.
- As the content of 2,4'-MDI in SMPU increases, proof strength total elongation and Young's modulus decrease.
- These results are attributed to the reduction in hard segment stacking caused by the ortho structure in benzene.

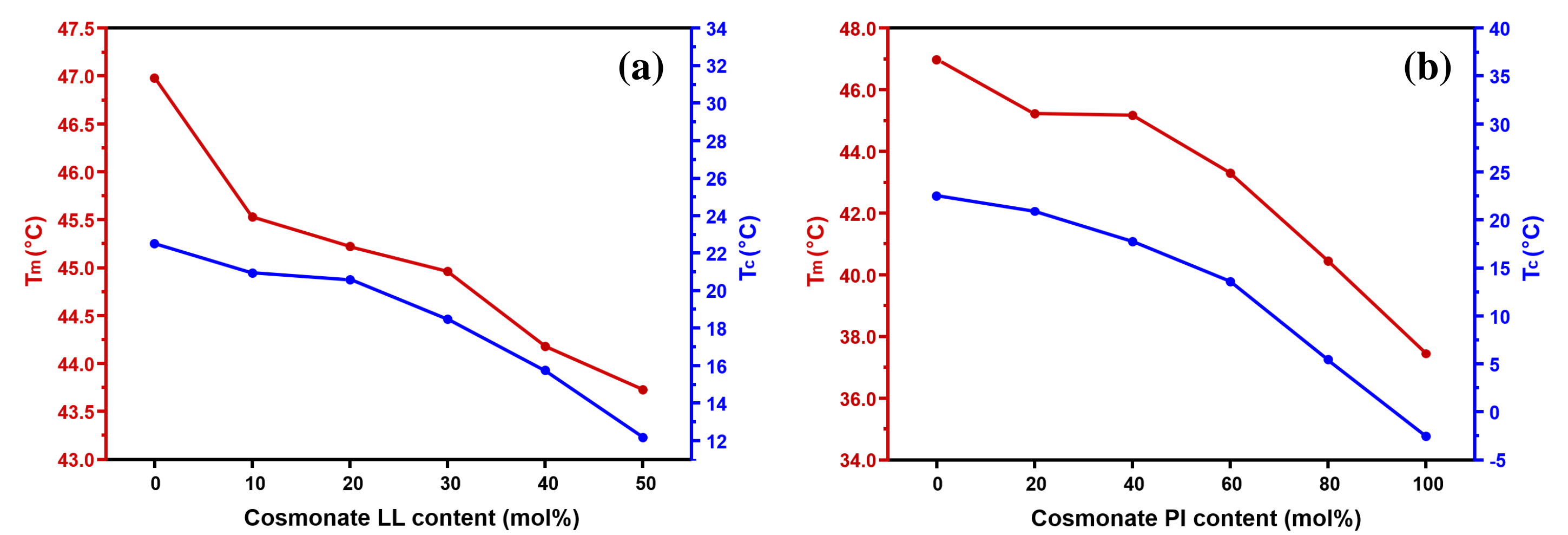


Figure 5. (a) T_m , T_c of the synthesized SMPU samples as a function of Cosmonate LL content in the isocyanate mixtures. (b) T_m , T_c of the synthesized SMPU samples as a function of Cosmonate PI content in the isocyanate mixtures.

- The test was conducted with DSC.
- As the content of MDI containing uretonimine linkage in SMPU increases, both T_m and T_c decrease. These results occur due to the uretonimine linkage at the center which leads to a decrease in the separation between the soft segment and the hard segment.
- As the content of 2,4'-MDI in SMPU increases, both T_m and T_c decrease. These results are attributed to interference of crystallinity by the ortho structure in benzene.

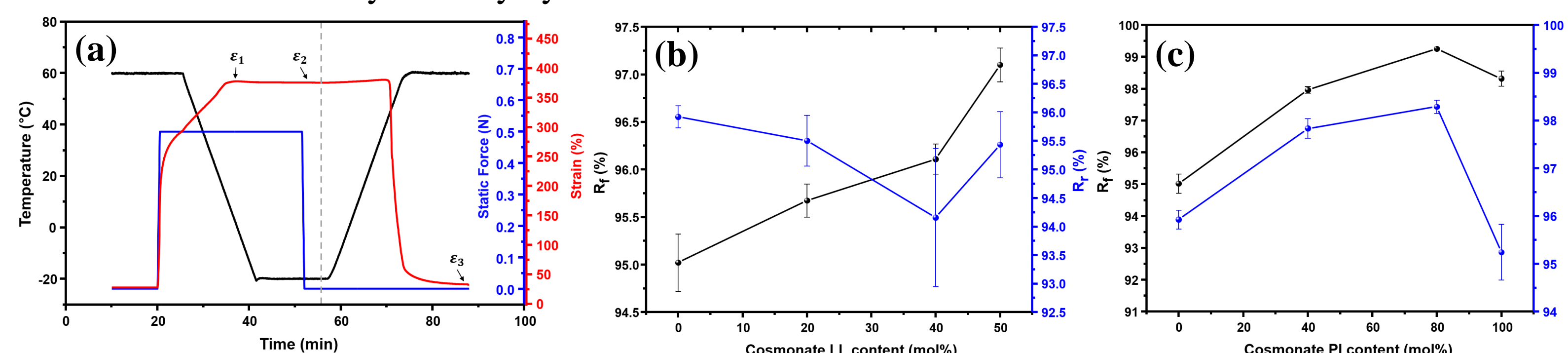


Figure 6. (a) A typical shape memory behavior of the SMPU from DMA analysis. (b) R_f and R_r values of SMPU samples as a function Cosmonate LL contents (c) R_f and R_r values of SMPU samples as a function Cosmonate PI contents.

- The test was conducted with DMA.
- As the content of Cosmonate LL increases, the hard segment becomes bulkier, showing a trend of increasing R_f values.
- Due to the increase in uretonimine, the interactions between the soft segment and hard segment relatively increase, causing the R_r to decrease. However, the R_r slightly increases due to entanglement.
- As the content of Cosmonate PI increases, the less mobile 2,4'-MDI structure in the SMPU would maintain its structure at low temperatures, thus resulting in a favorable condition. As a result, the decrease in the difference between ϵ_1 and ϵ_2 led to higher R_f value.
- Due to the increase in ortho-structured MDI, the elasticity increased, leading to a rise in the R_r value. However, with the excessive decrease in the hard segment, the material stretched excessively, resulting in a decrease in the R_f value.

$$R_f = \frac{\epsilon_2}{\epsilon_1} \times 100(\%)$$

$$R_r = \frac{\epsilon_2 - \epsilon_3}{\epsilon_2} \times 100(\%)$$

ϵ_1 : the maximum strain under the static force
 ϵ_2 : the strain at the temporarily fixed state
 ϵ_3 : the strain after shape recovery

References

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