Materials Today Chemistry 26 (2022) 101141

Contents lists available at ScienceDirect

### Materials Today Chemistry

journal homepage: www.journals.elsevier.com/materials-today-chemistry/

### Topologically designed cross-linking network for stretchable and recoverable pressure-sensitive adhesives with exceptional softness

M.-B. Yi<sup>a</sup>, T.-H. Lee<sup>a</sup>, S.-J. Lee<sup>a</sup>, J.-S. Kim<sup>a</sup>, H.-J. Kim<sup>a, b, \*</sup>

<sup>a</sup> Program in Environmental Materials Science, Department of Agriculture, Forestry and Bioresources, Seoul National University, Seoul 08826, Republic of Korea

<sup>b</sup> Research Institute of Agriculture and Life Sciences, Seoul National University, Seoul 08826, Republic of Korea

#### ARTICLE INFO

Article history: Received 10 March 2022 Received in revised form 25 May 2022 Accepted 11 August 2022 Available online xxx

Keywords: Topological cross-linking Sliding effect Slide-blocking units Strain stiffening Cyclodextrins

#### ABSTRACT

There is an increasing demand for soft-electronic devices. Such devices require adhesives that demonstrate appropriate stretching and recovery to support the assembly of various parts. The adhesives need to avoid plastic deformation and adhesion failure under repeated stretching. However, stretchable adhesives with covalent cross-linked polymer network and inorganic fillers have limitations in softness and adhesion performance, which is due to the hinder of chain mobility. Thus, providing elasticity without the compensation of chain mobility is strongly required. In this study, we introduced slide-blocking units to movable cross-linked polymers to improve the elasticity. The topologically designed cross-linking network causes a strain stiffening effect in the adhesives, showing outstanding softness, adhesion performance, and mechanical properties. Furthermore, the adhesives with the unique cross-linking network exhibited excellent stretching and recovery properties.

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### 1. Introduction

After Goodyear's discovery of cross-linking in natural rubber by using sulfur in 1839, cross-linking has been the most important approach to controlling the mechanical properties of polymers [1,2]. Although many factors affect the mechanical properties of polymers, such as monomers, molecular weight, cross-linking, and non-covalent interactions (e.g., van der Waals force, H-bond, and  $\pi$ - $\pi$  interaction) [3–7], cross-linking is the simplest and most effective variable for altering the polymer characteristics [8,9]. The presence of cross-links between polymer chains can enhance their elastic modulus and strength [10,11]. However, they can deteriorate the extensibility and toughness of polymers, as a trade-off factor [12,13].

In the 4th industrial revolution, soft electronics (e.g., flexible displays, biosensors, and electronic skin) have been gaining attention for their utilization in advanced applications to improve human life [14–17]. As an essential requirement of soft electronics, the pressure-sensitive adhesives (PSAs) used must demonstrate appropriate stretching and recovery to support the assembly of various parts [18]. Elasticity in adhesives should be improved to

\* Corresponding author. E-mail address: hjokim@snu.ac.kr (H.-J. Kim). minimize the plastic deformation after repeated folding or stretching. A simple way to enhance the elasticity is making a dense cross-linking network or adding inorganic fillers. Recently, there has been some research to obtain stretchable and recoverable pressure-sensitive adhesives by providing a robust cross-linking network or adding inorganic fillers [14,15,19]. However, densely cross-linked polymer chains, or polymer chains with low flexibility, have a limitation of chain mobility in microscopic view and cause a loss of softness and adhesion performance [9,20]. Further, the excessively stiffened adhesives hindered the stress dispersion of soft electronics during the deformation and originate an adhesion failure [21]. Therefore, a new approach is required to overcome the limitations.

Different from covalent cross-linking (chemical cross-linking), supramolecular interactions (physical cross-linking) have received increasing attention [22–24]. Adhesives with the supramolecular interactions exhibit enhanced mechanical properties [25–27] and unconventional functionalities such as underwater adhesion [28,29], selective interaction [30,31], and switchable adhesion [32]. However, physical cross-linking is also under the trade-off relationship between elasticity and viscosity owing to the hindered chain mobility [4,33]. As another cross-linking system, Ito et al. reported topological cross-linking based on poly-rotaxane [24], which resembles a necklace with cyclodextrins threaded onto PEG [34,35]. The cyclodextrins could slide through the PEG molecules.







and this sliding effect resulted in the exceptional stretchability and toughness of the polymers [36–39]. In addition, a movable crosslinker, modified cyclodextrins with acrylate functionality, has been developed by Takashima et al. [40–42] The movable crosslinker demonstrated in-situ threading onto the backbone chain (e.g., polyacrylate) during polymerization, resulting in a sliding effect as observed in poly-rotaxane. Our previous paper reported that the PSAs with movable cross-linker exhibited exceptional stretching and adhesion performances [42]. However, as the crosslinking is movable, the elasticity in the PSAs was insufficient to resist the plastic deformation against the external stretching [43].

Herein, we applied a topologically designed cross-linking network containing slide-blocking units in movable cross-linked polymers to obtain stretchable and recoverable PSAs with an exceptional softness (Scheme 1).

#### 2. Results and discussion

# 2.1. Strain stiffening effect owing to slide-blocking units in movable cross-linked PSAs

In our previous report [42], a modified  $\beta$ -cyclodextrin was used as a movable cross-linking agent. However, to maximize the sliding effect, we investigated  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin with different cavity sizes ( $\alpha$ -CD: 4.7–5.3 Å,  $\beta$ -CD: 6.0–6.5 Å, and  $\gamma$ -CD: 7.5–8.5 Å) as the sources of movable cross-linkers (Figures S1 and S2) [44]. The elongations at the break of PSAs were 2050% for  $\alpha$ 50 (0.50 mol% of  $\alpha$ -CD-AOI) and 2550% for  $\beta$ 50 (0.50 mol% of  $\beta$ -CD-AOI). However,  $\gamma$ 50 (0.50 mol% of  $\gamma$ -CD-AOI) did not exhibit an apparent fracture in our test limit (~3200%), indicating that the sliding effect of  $\gamma$ -CD-AOI is superior because of its largest cavity size. Hence, we adopted  $\gamma$ -CD-AOI as the movable cross-linker for this study. However, the sliding effect in the movable cross-linker pSAs hinders stress accumulation, resulting in plastic deformation of polymers. Thus, we added slide-blocking units to restrict the slidable area and achieve a strain stiffening effect. The strain stiffening is a unique mechanical behavior that enables polymers to exhibit low elastic modulus at low strain with the rapidly increased modulus at large deformations, like the mechanical behaviors of skin and organs [45]. In addition, the strain stiffening behavior is an effective strategy for obtaining tough and stretchable polymers with high recovery.

The mechanical properties of the PSAs with covalent crosslinking network (CCN), movable cross-linking network (MCN), and confined sliding network (CSN) were investigated via stressstrain curves from tensile tests (Fig. 1). The PSAs with 0.05 mol% of 1,6-hexanediol diacrylate (HDDA), named CCN05, exhibited a Young's modulus of 2.54 kPa. The Young's modulus increases with a higher amount of HDDA, and the PSAs with 0.20 mol% of HDDA (CCN20) exhibited a Young's modulus of 37.0 kPa, which is 14 times higher than that obtained for CCN05 (Table S1). In addition, the elongation at break decreased steeply from 2850% for CCN05 to 440% for CCN20. This tendency is typical in covalent cross-linking as the stress is inversely proportional to M<sub>c</sub> (average molecular weight between cross-linking points) and stiffer polymers are less stretchable [43,46]. Besides, the PSAs with fumed silica (CCN05\_Silica, CCN10\_Silica) showed decreased elongation at break and higher Young's moduli compared to CCN05 and CCN10, respectively. In contrast, PSAs with 0.15, 0.30, and 0.50 mol% of  $\gamma$ -CD-AOI (MCN15, MCN30 and MCN50), movable cross-linking network did not demonstrate an increase in the Young's moduli, and the elongations at break were beyond our test limit. Although the PSAs with movable cross-linking exhibited superior stretchability in tensile tests, they are weak to plastic deformation owing to their poor elastic property (Figure S3). We introduced slideblocking units into the movable cross-linked PSAs to get the strain stiffening effect, restricting the sliding of  $\gamma$ -CD-AOI in the polymer network. An appropriate amount of HDDA (0.05 mol%) was added to the PSAs with 0.15, 0.30, and 0.50 mol% of  $\gamma$ -CD-AOI (CSN15, CSN30, and CSN50, respectively), confined sliding network.



Scheme. 1. Illustration of a) the synthetic process of movable cross-linker and b) the topologically designed cross-linking network with slide-blocking units in the movable cross-linked polymers (confined sliding network).



**Fig. 1.** Stress-strain curves of a) PSAs with Covalent Cross-linking Network (0.05–0.20 mol% of HDDA, CCN05 – CCN20), silica added PSAs (CCN05\_Silica, CCN10\_Silica), b) Movable Cross-linking Networked PSAs (0.15–0.50 mol% of γ-CD-AOI, MCN15 – MCN50) and Confined Sliding Networked PSAs (0.15–0.50 mol% of γ-CD-AOI with 0.05 mol% of HDDA, CSN15 – CSN50). c) Young's modulus and d) tensile strength of PSAs from stress-strain curves.

The strain stiffening effect was observed at 1500–2500% strain owing to the presence of the slide-blocking units, and this stiffening was shown earlier for a higher amount of  $\gamma$ -CD-AOI (Fig. 1b). The slide-blocking units accumulate stress, and a higher amount of  $\gamma$ -CD-AOI reduces the slidable area [47]. However, the addition of slide-blocking units to  $\gamma$ -CD (without acrylate functionality) did not alter its mechanical properties due to the absence of cross-linking (Figure S4).

Young's moduli and tensile strength of PSAs were analyzed to investigate the differences among the various cross-linking network (Fig. 1c and d). To compare the effects of cross-linking networks, cross-linking density was calculated via the Flory-Rhener equation by swelling the PSAs in acetone (Figure S5). The Young's moduli of covalently cross-linked PSAs (CCN05 to CCN20) exhibit a linear dependency with increased cross-linking density. and the addition of fumed silica caused an additional modulus increase. However, the movable cross-linked PSAs (MCN15, MCN30, and MCN50) and the PSAs with  $\gamma$ -CD (without acrylate functionality) and slide-blocking units exhibit a negligible increase in crosslinking density and Young's moduli; this may be owing to the sliding of  $\gamma$ -CD-AOI and the no-formation of cross-linking for  $\gamma$ -CD. Notably, the confined sliding networked PSAs, which have the limited sliding area of  $\gamma$ -CD-AOI, show increased cross-linking densities and Young's moduli with the addition of  $\gamma$ -CD-AOI, exhibiting a similar linear dependency with covalent cross-linking.

This change would originate from the slide-blocking of  $\gamma$ -CD-AOI, making a stress accumulation in the deformation process. The untrapped cyclodextrin (free slidable) ratio is ten times higher than trapped cyclodextrin (sliding hindered) in the movable cross-linking network [48]. Thus, the addition of slide-blocking units makes the untrapped  $\gamma$ -CD-AOI behave like trapped cyclodextrins, thereby providing elasticity.

The tensile strength of covalent cross-linked PSAs showed a linear decrease depending on the cross-linking density. The tensile strength of CCN05 was 455 kPa, and it decreased to 232 kPa for CCN20. However, despite the increased elasticity, the tensile strengths of confined sliding networked PSAs were increased to 621 kPa for CSN15, 859 kPa for CSN30 and 764 kPa for CSN50. In addition, the PSAs maintained considerably high fracture energies (~404 MJ/m<sup>3</sup> for CSN50), and CSN30 exhibited slightly higher fracture energy (516 MJ/m<sup>3</sup>) than that of CCN05 (504 MJ/m<sup>3</sup>) (Figure S6). The superior strength and toughness are due to the strain stiffening behavior, showing that the sliding effect of  $\gamma$ -CD-AOI is still effective in the network [47].

# 2.2. Rheological properties and polymer chain mobility for confined sliding network

We investigated the rheological properties of PSAs to determine the changes in the shear modulus according to their cross-linking

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Fig. 2. Rheological properties for PSAs with various cross-linking networks. The storage modulus of PSAs for a) covalent cross-linking (CCN), b) movable (MCN) and confined sliding network (CSN). The loss factors include c) covalent cross-linking (CCN), d) movable (MCN) and confined sliding network (CSN).

structures (Fig. 2). The inclusion of covalent cross-linking makes the storage moduli higher, and a plateau-like region is observed for CCN20 in the low frequencies ( $\omega = 0.01-1 \text{ s}^{-1}$ ) [49,50]. However, the PSAs with movable cross-linking (MCN30 and MCN50) show lower moduli changes than covalently cross-linked PSAs. The sliding effects from  $\gamma$ -CD-AOI likely cause stress dissipation dominantly at low frequencies because of the slow relaxation between the movable cross-linker and backbone chains [48,51]. With the addition of slide-blocking units, CSN15, CSN30, and CSN50 exhibited increased moduli in the low frequencies, proportionally to the amount of  $\gamma$ -CD-AOI. This modulus increase can be correlated with Young's moduli of the PSAs in Fig. 1, indicating that the slideblocking units provide elasticity to the PSAs by restricting the slidable area of  $\gamma$ -CD-AOI. However, further investigations, such as molecular simulations and calculations based on polymer elasticity, should be conducted to verify the confined sliding network's elasticity strictly.

Loss factor  $(\tan \delta)$ , as an indicator for the fluidity of polymer, was investigated to compare the effect of the cross-linking network to chain mobility (Fig. 2c and d). The addition of covalent cross-linking caused a significant decrease in the loss factor due to the fixed chain configuration, and the hindered chain mobility would be the reason for decreased elongation at break and poor adhesion of PSAs with covalent cross-linking. However, the loss factors of movable and confined sliding networked PSAs were considerably higher than those of the covalently cross-linked PSAs. The loss moduli (G") of movable and confined sliding networked PSAs did not change significantly, and the increase in their storage moduli (G') was smaller than those of the PSAs with covalent cross-linking. The sliding effect of  $\gamma$ -CD-AOI in the polymer network likely enables the retention of chain mobility in PSAs despite the cross-linking, thereby resulting in a lower storage modulus (G') and higher loss factor (tan  $\delta$ ).

The glass-transition temperature (Tg) of the PSAs (Fig. 3) was investigated to determine changes in the segmental mobility of the polymers. The  $T_g$  for PSAs without cross-linking (Pristine) is -45.3 °C, which is close to that calculated using the Fox equation (–48.2 °C,  $T_g$  for pBA: –54 °C, pHEA: 4 °C) [52]. The addition of covalent cross-linking resulted in a minor change in Tg (CCN20: -44.9 °C), which indicates that the segmental mobility of polymer chains is not hindered significantly. However, the addition of  $\gamma\text{-CD-AOI}$  increased  $T_g$  to  $-41.0\ ^\circ\text{C}$  for MCN50. This increase is attributed to high Tg of cyclodextrins molecules [48,53,54]. Typically, lower Tg means softness of polymers, showing higher segmental mobility of polymer chains. However, the PSAs with confined sliding network (MCN and CSN) demonstrated higher elongation at break and lower Young's modulus in the tensile and rheological tests despite their higher Tg compared to CCN. We thought that the major contributor of the superior mechanical properties is the topologically designed cross-linking network and the flexibility of polymer network is more dominant for softness than segmental motion.



Fig. 3. Glass-transition temperature of PSAs with a) covalent cross-linking (CCN), b) movable (MCN) and confined sliding network (CSN) determined by differential scanning calorimetry (DSC) measurements.

2.3. Adhesion performances of PSAs with the confined sliding network

Tackiness, the adhesion force obtained in a short duration (~1s), is a major requirement for the proper adhesion of PSAs on the adherent. In addition, rheological characteristics could be derived from tackiness [55,56]. The pristine sample exhibited a large

deformation distance by fibrillation during the detaching in the probe tack test (Fig. 4a and b). However, the fibrillation decreased sharply with the addition of covalent cross-linking, and the maximum probe tack was 6.0 N for CCN10, and the tackiness was slightly less for CCN15 and CCN20 (Table S2). The work of adhesion is 341 kJ/m<sup>2</sup> for Pristine, and it decreased with an increase in the amount of HDDA (CCN20: 82 kJ/m<sup>2</sup>). The poor tackiness and work



Fig. 4. Adhesion performances of PSAs. Probe tack test for PSAs with a) covalent cross-linking network (CCN), b) movable (MCN) and confined sliding network (CSN). Peel strength of PSAs with c) covalent cross-linking network (CCN), d) movable (MCN) and confined sliding network (CSN).



Fig. 5. A lap shear adhesion test for PSAs with a) covalent cross-linking (CCN), b) movable (MCN), and confined sliding network (CSN), c) A scheme of lap shear adhesion test specimen.

of adhesion for covalent cross-linking is likely owing to the limited fibrillization [57]. However, the movable cross-linked and confined sliding networked PSAs exhibited enhanced tackiness and work of adhesion. The topological cross-linking owing to  $\gamma$ -CD-AOI enhances the cohesive interactions, and the sliding effect provides sufficient stretchability for fibrillization. However, H05 $\gamma$ "30 (0.05 mol% of HDDA and 0.30 mol% of  $\gamma$ -CD) does not exhibit a notable change in tackiness as compared to that of CCN05 (Figure S7). These results show that the co-existence of acrylate functionality in the movable cross-linker is essential for topological cross-linking.

Peel strengths were investigated as another principal adhesion factor (Fig. 4c and d). Peel strength is strongly dependent on the balance between adhesion and cohesion, and cross-linking is the most significant factor for this balance [9,20]. For covalently crosslinked PSAs, the peel strength decreases with the addition of HDDA. The enhanced cohesive interactions owing to HDDA restrict the chain flexibility of polymers, as evident from the hindered fibrillation observed in the probe tack test. In addition, the stiffened chains deteriorate the stress dissipation during the detaching process, resulting in decreased peel strength. As a result, CCN20 demonstrated a poor adhesion performance (4.3 N/25 mm), lower than the commercial PSAs (6.5 N/25 mm, Scotch 309 from 3 M). In addition, the silica-containing PSAs showed a similar result with the covalently cross-linked PSAs due to the stiffened network (Figure S8). However, the PSAs with movable cross-linking (MCN30) demonstrated superior peel strength (33.6 N/25 mm), which agrees with our previous report [42]. This superior peel strength is owing to the sliding effect of  $\gamma$ -CD-AOI, which strengthens the cohesive interactions in polymers while enabling the retention of chain mobility. Further, the confined sliding networked PSAs did not cause the decrease of peel strengths despite the increased  $\gamma$ -CD-AOI; they maintained considerable peel strength (~13 N/25 mm) despite the high concentration of  $\gamma$ -CD-AOI (0.50 mol%, CSN50). This tendency is not common for conventional cross-linking because of the trade-off relationship between elasticity and viscosity It might originate from the topologically designed cross-linking network, providing softness and toughness.

## 2.4. Stretching and strain recovery test for PSAs with confined sliding network

When using soft electronics, bending and folding occur frequently, and the layers in the device suffer shear stress and elongation [18,21]. Therefore, all the components of soft electronics

should withstand the repeated shear stress without malfunctions [16,58]. The adhesives, an essential part of their assembly, must possess sufficient stretchability and withstand the shear stress during deformation. If the adhesives cannot withstand appropriate shear stress and elongation, delamination or defects could appear in the soft electronics [18]. To compare the mechanical properties at shear stress for the various cross-linking systems, we conducted a lap shear test on the PSAs. (Fig. 5, Fig. S9 and Table S3).

The covalently cross-linked PSAs exhibit a sharp decrease in elongation and a negligible increase in the shear strength, similar to that observed in the tensile test (Fig. 1). However, the movable cross-linked and confined sliding networked PSAs exhibited enhanced shear strength with an increase in  $\gamma$ -CD-AOI. The shear strength of MCN50 and CSN50 are 129.7 and 133.8 kPa, respectively, which are more than 30% higher than CCN10 (99.0 kPa). The sliding effects from  $\gamma$ -CD-AOI likely aid stress dissipation during deformation, resulting in superior adhesion performance [38,42,47].

To determine the stretchability and recovery of the PSAs, we conducted a strain-recovery test (Fig. 6 and Fig. S8). Shear stress was applied to achieve the desired strain and was removed to observe the recovery after deformation. The PSAs without crosslinking could not withstand the shear stress during deformation because of the weak cohesive forces, and they exhibited adhesion failure in the tests. For CCN05, adhesion failure is not observed until 1200% shear strain; however, the recovery after the deformation was poor (under 70%) for the strain range. The poor recovery is attributed to insufficient elasticity because of the incomplete crosslinking network of CCN05. For the PSAs with a higher cross-linking density (CCN10), the recovery was significantly improved to ~90% for 300 and 600% strain. However, CCN10 could not withstand higher elongation (over 600%) owing to its stiff cross-linking network. The PSAs with movable cross-linking, MCN30, exhibited high stretchability (~1200%) and superior stress relaxation properties (~80%) for all ranges owing to the considerable stress dissipation ability from the sliding effect [38]. However, the stress dissipation restricts the elasticity of polymers, as indicated by the poor strain recovery (~50% for MCN30), which could result in severe plastic deformation after the stretching process. In contrast, the confined sliding networked PSAs (CSN30) exhibit superior elongation at 1200%, and the recovery was above 80% for all the strains. The softness of the PSAs makes the adhesion stable during the stretching, and the toughness from the strain stiffening effect achieves remarkable recovery.

Plastic deformation or adhesion failure for repeated deformation was investigated using a folding apparatus by applying a cyclic



**Fig. 6.** Strain-recovery properties of PSAs with a), b) covalent cross-linking (CCN, 0.05 and 0.10 mol% of HDDA), c) movable (MCN, 0.30 mol% of γ-CD-AOI), and d) confined sliding network (CSN, 0.05 mol% of HDDA & 0.30 mol% of γ-CD-AOI). Shear stress was applied to get the aimed shear strain in PSAs. The stress was maintained for 10 min and removed to see the recovery property during 10 min.



**Fig. 7.** Visual inspections of PSAs during cyclic stretching and recovery with a folding machine. a) preparation of folding specimens and optical images during the folding test. PSAs b) without cross-linking and with c) covalent cross-linking (CCN, 0.10 mol% of HDDA), d) confined sliding network (CSN, 0.05 mol% of HDDA as slide blocking units and 0.30 mol% of γ-CD-AOI). The folding was repeated to 100 k cycles, and the images of PSAs were obtained for every 5 k cycles with an optical microscope.

strain (100 k) (Fig. 7). The PSAs were laminated between 50  $\mu$ m PET and folded with a 3 mm radius. The estimated shear strain experienced by the PSAs was 500–700% [18]. The PSAs without cross-linking (Pristine) exhibited permanent deformation parallel to the folding line after 20 k cycles. After 100 k cycles, the deformation became severe, and delamination occurred. The plastic deformation is mainly attributed to the low elasticity of PSAs owing to the absence of cross-linking. On the other hand, a crack was observed for CCN10 in the early stages of the cyclic test (5 k cycles). In addition, the crack was enlarged during the test, indicating the critical delamination of adhesives after 100 k cycles. Stiff network from the strict covalent cross-linking may result in crack formation under repeated strain.

Notably, PSAs with the topologically designed network (CSN30) exhibited an entirely defect-free state after 100 k cycles. This result indicates that CSN30 retains its stretchability and recovery even after 100 k repeated deformation. Consequently, we propose that introducing the confined sliding network in PSAs is one of the most effective approaches for obtaining stretchable and recoverable adhesives.

#### 3. Conclusions

We developed stretchable and recoverable adhesives with exceptional softness by adding slide-blocking units to movable cross-linked polymers. The topologically designed cross-linking structure (confined sliding network) caused a strain stiffening effect in PSAs, which resulted in an outstanding improvement in tensile strength and fracture energy despite the low elastic modulus. Though the slide-blocking units enhanced the polymers' elasticity, the polymer chain's fluidity was considerable because the sliding effect of  $\gamma$ -CD-AOI was still effective in the network. The PSAs with the confined sliding network showed superior stretchability and recovery without an adhesion failure or major plastic deformation during the repeated stretching. The trade-off relationship between elasticity and viscosity in adhesives was overcome via the topological design. However, in this study, the stretchability and recovery of PSAs were restricted to the shear direction. Therefore, stretchable PSAs for tensile direction need to be studied further. Nevertheless, the topological design for crosslinking is a viable approach to synthesizing advanced polymers for many applications (e.g., stretchable substrate, bio patch, artificial organs, etc.) beyond the adhesives.

#### 4. Experimental section

*Materials*: Butyl acrylate, dibutyltin dilaurate (DBTDL), and 1,6hexanediol diacrylate (HDDA) were purchased from Sigma-Aldrich (USA). 2-hydroxyethyl acrylate, acetic anhydride, and pyridine were purchased from Samchun (Korea). Cyclodextrins ( $\alpha$ -CD,  $\beta$ -CD, and  $\gamma$ -CD) were purchased from TCI (Japan). 2isocyanatoethyl acrylate (AOI) was purchased from Showa Denko (Japan). Acetone, DMF, and DI water were purchased from Daejung (Korea). The Omnirad 1173, a photoinitiator (PI), was purchased from IGM (Netherlands).

Synthesis of a supramolecular movable cross-linker: The movable cross-linker, named  $\gamma$ -CD-AOI, was prepared by modifying the previously reported method [42]. In this report,  $\gamma$ -CD was used as a precursor for the movable cross-linker. First, a urethane reaction was conducted between the hydroxyl group of  $\gamma$ -CD and the iso-cyanate group of AOI to attach the acrylate functional group to  $\gamma$ -CD. Then, the prepared  $\gamma$ -CD-AOI was acetylated by acetic anhydride to make it soluble in acrylate monomers. The AOI attachment and acetylation of  $\gamma$ -CD-AOI were characterized by the FT-IR spectrum (Figure S10). The average number of AOI substituted to

 $\gamma$ -CD was confirmed to be 1 by the NMR spectrum (Figures S11 and S12).

Preparation of pre-polymer and pressure-sensitive adhesives (PSAs): A pre-polymer was prepared to get enough viscosity for a coating step. Butyl acrylate (0.9 mol) and 2-hydroxyethyl acrylate (0.1 mol) were added to a three-neck flask with a photoinitiator (3 mmol). The mixture was purged with nitrogen gas for 15 min and irradiated by a UV light (100 mW/cm<sup>2</sup>) for 30 s with mechanical stirring. The polymer ratio in the pre-polymer (10.1 wt%) was characterized by TGA (Figure S13), and the molecular weight of the polymer was characterized by GPC (Mn: 898 kDa, Mw: 1275 kDa, and PDI: 1.42). Pressure-sensitive adhesives were prepared by curing the pre-polymer. An additional photoinitiator (0.2 mol%) and various amounts of the cross-linking agent were added to the pre-polymer. Then, the mixture was coated on a silicone release film by a film applicator (100 µm-thickness). Finally, the coated solution was irradiated by a UV LED lamp (Intensity =  $30 \text{ mW/cm}^2$ ) for 2 min to obtain fully cured polymers.

Characterizations: The IR spectra were measured using the FT-IR spectrometer (Nicolet iS20, Thermo Fisher Scientific) by attenuated total reflection (ATR) mode. The <sup>1</sup>H-NMR, <sup>13</sup>C-NMR were recorded by 600 MHz NMR spectrometer (AVANCE 600, BRUKER) at 25 °C. In all the NMR measurements, chemical shifts were referenced to an internal standard ( $\delta = 0$  ppm for tetramethylsilane). The molecular weight and polydisperse index of polymers were measured by gel permeation chromatography (1100 S, Agilent). The specimens were dissolved in tetrahydrofuran with a 1 mg/mL concentration. The flow rate was 1 mL/min, and the refractive index detector was used for detection. A PMMA standard was used for the calibration. The polymer ratio of the pre-polymer and the PSAs were measured using a thermogravimetric analyzer (TGA4000, PerkinElmer). 20-30 mg of specimens were mounted and heated to 500 °C from 25 °C with a rate of 10 °C/min. The tensile tests of the PSAs were conducted using a texture analyzer (TA-XT plus, Stable Micro System) with a 300 mm/min crosshead rate at 25 °C. The PSAs with  $80 \,\mu\text{m}$  thickness were cut to  $25 \times 25 \,\text{mm}^2$ , and the PSAs were rolled up to make cylindrical shapes with a 2 mm<sup>2</sup> cross-section area. The cylindrical specimens were used for tensile tests to investigate the mechanical properties of the PSAs (Figure S1). The glass-transition temperature (Tg) was measured using a differential scanning calorimetry (DSC Q200, TA Instruments). 8-10 mg specimens were heated to 100 °C from room temperature at a rate of 10 °C/min. Then, the specimens were quenched to  $-80 \degree C$  and held for 15 min. Finally, they were heated to 100 °C at a rate of 2 °C/min. The  $T_{\rm g}$  was calculated from the final step. The peel and probe tack tests were conducted using a texture analyzer (TA-TX plus, Stable Micro System) at 25 °C. Peel strength was measured with a 300 mm/min crosshead rate at an angle of  $180^\circ$ . The 50  $\mu$ m PET film was used as a backing film, and the PSAs were attached to a glass substrate. The PSAs were then pressed 4-times with a 2 kg roller and dwelled for 20 min before the peel tests. Probe tack was measured with a 5 mm SUS cylinder probe at a constant detaching rate of 10 mm/s after a 100 g/cm<sup>2</sup> force with 1 s contact time. The rheological properties were measured using a rheometer (ARES-G2, TA Instruments). A disposable aluminum round plate of an 8 mm diameter was used. The shear rate was  $0.01-100 \text{ s}^{-1}$ , and all tests were conducted by 1.0% strain. The rheological tests' specimens were prepared with a thickness of 300–350 µm by laminating the PSAs. The lap shear and recovery tests were conducted using a dynamic mechanical analyzer (Q800, TA Instruments) equipped with a tension clamp at 25 °C. The PSAs were attached to a poly (methyl methacrylate) substrate (20  $\times$  6 mm) with a 10  $\times$  6 mm<sup>2</sup> adhesion area, and a shear force was applied to the specimen with a ramp of 1 N/min. For the recovery tests, shear stress was applied to the PSAs to generate a specific strain, and the strain was maintained for 10 min.

Subsequently, the stress was released to investigate the recovery for 10 min. The cyclic stretching and recovery properties of the PSAs were measured using folding apparatus (Foldy-100, FlexiGo, Korea). The radius of curvature was 3 mm, and the experiment was performed at 30 cycles per minute and 25 °C. The 80  $\mu$ m-thick PSAs were laminated between 50  $\mu$ m PET films. The specimens were then attached to a folding plate using adhesives. The folding was then repeated for 100 k cycles. The conditions of the PSAs during the cycles were observed via optical microscopy.

#### Credit author statement

Mo-Beom Yi: Conceptualization, Methodology, Data Curation, Writing. Tae-Hyung Lee: Conceptualization, Methodology. Seong-Ju Lee: Methodology, Investigation. Ji-Soo Kim: Methodology. Hyun-Joong Kim: Supervision.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgment

We want to thank FlexiGo and Anyone for free support of the cyclic folding and rheological tests. This work was financially supported by Samsung Display Co.,Ltd.

#### Appendix A. Supplementary data

The Supporting Information is available free of charge on the ACS Publications website.

Tensile test of PSAs; cross-linking density calculation; probe tack test; peel test; lap shear test; strain-recovery test; FT-IR spectra of materials; NMR spectroscopy of synthesized materials; thermogravimetric analysis.

Cyclic folding test (MOV).

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtchem.2022.101141.

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