Solvent-free polyurethane adhesives with excellent adhesion performance at ultra-low temperature

Kyung-Min Kim, Jong-Ho Back, Hyun-Joong Kim

Abstract

Adhesives with excellent adhesion and high elongation at cryogenic temperatures are necessary for fields such as aerospace, transportation, superconductors, and medicine, but have difficult requirements. This study aimed to develop a solvent-free, two-component polyurethane (PU) adhesive with excellent adhesion and high elongation, especially in ultra-low temperature conditions. We incorporated bulky polydimethylsiloxane (PDMS) diol into the hard segment of the PU adhesive to enhance flexibility and improve physical cross-linking within the adhesive matrix. The resulting PDMS-based PU adhesive showed a tensile strength of 120 MPa at −170 °C and a high elongation of approximately 4%. It showed a lap-shear strength of up to 13 MPa at −196 °C. Additionally, the adhesive was curable at 23 °C. In this study, the cryogenic applicability of the PU adhesive was evaluated at −170 °C (103 K, liquid natural gas) and −196 °C (77 K, liquid nitrogen). Future research on the polymer adhesive materials applicable to ultra-low temperatures, such as 20 K, may be necessary if storage and transportation of liquid hydrogen become feasible.

1. Introduction

Adhesives with excellent adhesion and high elongation at cryogenic temperatures are necessary for fields such as aerospace, transportation, superconductors, and medicine, but have difficult requirements. Polymer-based materials must exhibit cold resistance, durability, low thermal expansion rate, and excellent fatigue performance. Most polymer-based adhesive materials are brittle, and their adhesive performance deteriorates significantly with decreasing temperature because of the macroscopic structural changes. Thermosetting epoxy resin is durable and can maintain excellent adhesion at extremely low temperatures. However, due to its chemically cross-linked network structure, its flexibility is poor at low temperatures. To solve this problem, many efforts have been made to develop adhesive materials that have excellent mechanical properties and flexibility at ultra-low temperatures. Recently, the influences of anti-freezing features, supramolecular structure, and irreversible bonding on the properties of cryogenic adhesive materials have been studied. However, anti-freezing using water–ethanol as a solvent is difficult to use at extremely low temperatures, and adhesives utilizing supramolecular structures and reversible bonds can be applied at extremely low temperatures, but their adhesive performance is poor. In particular, when the chemical cross-linking structure was strong, the adhesion was high at cryogenic temperatures, but the flexibility was too low. Therefore, we would like to research utilizing polyurethane adhesive materials with a microphase separation structure that are flexible and easy to control physical properties at cryogenic temperatures.

Its molecular structure must be flexible for polyurethane to have high elongation at ultra-low temperatures. The flexibility of a material is greatly influenced by the strength, arrangement, and degree of freedom of the intermolecular bonds. Niu et al. improved cryogenic physical properties by imparting specific flexibility to the molecular chain in a phase-separated structure, such as PU. Similarly, when polyurethane elastomer is made using PDMS, which has a long molecular weight and a large volume, in the polyurethane molecular chain, it has a high elongation at room temperature and excellent elastic properties at low temperatures. However, when flexibility is added to thermoplastic polyurethane, it has low adhesive strength at extremely low temperatures, and studies have been proposed to improve adhesive properties by utilizing physical cross-linking including hydrogen bonding. Therefore, in PU structures composed of hard and
soft segments, the microstructure of the hard segments is essential to achieve high adhesive properties [36–43]. However, to apply one-component polyurethane adhesives at cryogenic temperatures, residual solvent or water must be removed or it hardens for a long time at high temperatures and has poor storage stability. In particular, room temperature curing was a difficult condition.

We endeavored to create a solvent-free PU adhesive suitable for applications at ultra-low temperatures. Accordingly, an NCO prepolymer containing an NCO end group was prepared by combining 4,4′-methylene diphenyl diisocyanate (4,4′-MDI) with polydimethylsiloxane (PDMS) diol (a chain extender) and poly(tetrahydrofuran) (PTMEG). A prepolymer containing diisocyanate was selected as 4,4′-MDI, which contains a benzene ring, to enable room-temperature curing when manufactured as a two-component polyurethane adhesive. PDMS diol, characterized by its ability to rotate along the Si-O chain and its low Tg, played a crucial role in the formulation. As the synthesized prepolymer remained liquid at room temperature, it was blended with other components containing OH groups to produce a solvent-free, two-component PU adhesive capable of curing at ambient conditions. In conclusion, we developed a solvent-free, room-temperature curable PU adhesive with excellent elongation and adhesive strength at cryogenic temperatures by adding a bulky PDMS group to the hard domain area to provide flexibility and form a strong physical bond (Scheme 1).

2. Experimental section

2.1. Materials

PTMEG (M_n = ~650 g/mol, TCI, Japan), PDMS diol (M_n = ~550 g/mol, Sigma-Aldrich, USA), 44,4′-MDI (M_n = ~250.25 g/mol, Sigma-Aldrich, USA), dibutyltin dilaurate (DBTDL, 95 %, TCI, Japan), toluene (>99.8 %, Samchun Chemicals, Republic of Korea), acetic acid (anhydrous, Samchun Chemicals, Republic of Korea), di-n-butylamine (Samchun Chemicals, Republic of Korea), bromophenol blue (TCI, Japan), 4-dimethylaminopyridines (TCI, Japan), 0.5 mol/L-hydrochloric acid in methanol (Samchun Chemicals, Republic of Korea), acetone (99.7 %, Samchun Chemicals, Republic of Korea), and methanol (anhydrous, 99.8 %, Sigma-Aldrich, USA) were used without purification. Ruthenium tetroxide (RuO_4), 0.5 % solution in water (stabilized, Thermo Fisher Scientific, USA) was used for staining.

2.2. Synthesis of prepolymer

MDI was purged with N_2 at 50 °C for 1 h in a reaction chamber, followed by the gradual addition of PDMS diol. Subsequently, 10 ppm of DBTDL was introduced at 75 °C and stirred at a constant speed to enable the reaction for 6 h. When the expected NCO% was reached, PTMEG was added and allowed to react for 3 h. The prepolymers were named 0.1 BM, 0.24 BM, and 0.3 BM, based on the molar ratio of PTMEG to PDMS diol (PTMEG: PDMS = 1:0.1, 1:0.24, 1:0.3). In the case of BM (pristine), PTMEG was used directly without adding PDMS diol (Table S1) [36,43–50].

2.3. Preparation of two-component PU adhesives

The resin and prepolymer were mixed at a 1.1 NCO index (=NCO eq./OH eq.) through vacuum defoaming at 2,000 rpm and 80 kPa for 3 min using a paste mixer (ARV-310, Thinky, Japan). The PU adhesives were named PU-BM, PU-BM_{0.1}, PU-BM_{0.24}, and PU-BM_{0.3}, based on the prepolymer. The mixed solution was dried in a nitrogen environment at 23 °C and 50 % humidity for over 3 d, followed by post-curing at 80 °C for 3 h (Table S2).

Scheme 1. (a) Hydrogen bonding interaction of the two-component PU adhesive with hard and soft domains. (b) Preparation of prepolymer through a solvent-free approach.
2.4. Characterization of the prepolymer and two-component PU adhesives

$^1$H nuclear magnetic resonance (NMR) and $^{29}$Si NMR spectra were recorded on an Avance III HD (Bruker Optics, Germany) NMR spectrometer operated in the Fourier-transform mode with an operating frequency of 600 MHz at 25 °C. Chloroform was used as the solvent (Figure S1 and Figure S2).

The number-average molecular weight ($M_n$) and molecular weight distribution (PDI, $M_w/M_n$) of the prepolymer were determined through gel permeation chromatography (GPC, YL9100 HPLS, Young Lin Instrument Co., Ltd., Republic of Korea). The columns were calibrated against standard poly(methyl methacrylate) (PMMA) samples (Table S2).

The hydrogen bonds in the hard segment in the prepolymer and PU adhesives were investigated by attenuated total reflection Fourier-transform infrared spectroscopy (ATR FT-IR). The FT-IR spectra were collected between 4000 and 400 cm$^{-1}$ using a BERTEX80 FT-IR spectrometer ( Nicolet is20, North Billerica, Thermo Fisher Scientific, USA). The number of scans was 16, and the resolution was 4 cm$^{-1}$ (Figure S3).

The microphase separation of PU was observed using an FT-IR instrument. The hydrogen bonding between hard segments was strongly correlated with microphase separation. The vibrations arising from the hydrogen-bonded N-H or C=O band were investigated. The degree of phase separation (DPS) and hydrogen bonding index (HI) were calculated using Eqs. (2), (3), and (4) [51–53].

$$\text{DPS}_\text{H} = \frac{(N-H)\text{hydrogenbounded}}{(N-H)\text{free}}$$

$$\text{DPS}_\text{O} = \frac{(C=O)\text{hydrogenbounded}}{(C=O)\text{free}}$$

$$\text{HI} = \frac{(C=O)\text{hydrogenbounded}}{(C=O)\text{free}}$$

The relationship between absorbance and reactant concentration was defined using the Beer–Lambert law in Eq. (4).

$$A = \varepsilon b C$$

where $A$ is the measured absorbance, $\varepsilon$ is the extinction coefficient (L·cm$^{-1}$·mol$^{-1}$), $b$ is the thickness of the reactant, and $C$ is the concentration of the reactant (mol·cm$^{-3}$).

The strong stretching vibration band of the NCO group (2, 272 Si NMR (Figure S1 and Figure S2). The NCO band was investigated. The degree of hydrogenation was defined using the Beer-Lambert law (Eq. (4)).

$$A = \varepsilon b C$$

The ratio of the initial absorbance of the reaction ($A_0$) and absorbance at time $t$ ($A_t$) was transformed into the ratio of the initial concentration of the reaction ($C_0$) and the concentration at time $t$ ($C_t$) to calculate the conversion rate ($\alpha$), as shown in Eq. (6):

$$\alpha = \frac{C_0}{C_t} = -\frac{A_t}{A_0}$$

Differential scanning calorimetry (DSC) measurements were performed on a calorimeter (DSC-Q200, TA Instruments, New Castle, DE, USA). The sample was heated in a pan at a heating rate of 20 °C/min in two cycles (from –80 to 100 °C) under a nitrogen atmosphere. The weight of the sample was approximately 5 mg.

The temperature dependences of the dynamic storage modulus ($G'$) and tan δ values of the PU adhesives were evaluated through dynamic mechanical analysis (DMA, Q800, TA instruments, USA) in the shear sandwich mode over a temperature range of –90 to 200 °C at a heating rate of 5 °C/min, strain rate of 0.01 %, and frequency of 1 Hz. The dimensions of the specimens were 10 mm × 10 mm × 2 mm.

The tensile strengths of the PU adhesives were evaluated using a 20 kN universal testing machine (Z020, Zwick Roell, Germany) at a crosshead speed of 1.3 mm/s. Tensile specimens were manufactured using a metal molder, following ISO 527–2 1B standards. Specifically, the specimens were cured for more than 3 d in a nitrogen atmosphere at 23 °C and then post-cured for 3 h at 80 °C. Three specimens were tested for each condition.

The lap-shear test was conducted using a universal testing machine (Z020, Zwick, Germany) equipped with a 20 kN load cell and operating at a crosshead speed of 1.3 mm/min (ISO 4587). The joints were prepared using adhesives to bond two pieces of the substrate with a glued area of 12.5 mm × 25 mm. The substrate was CR 340 (cold roll steel) subjected to sandblasting and sonication cleaning in acetone for 30 min. The lap-shear test was conducted in triplicate, and the work of debonding was calculated using the integral of the force-displacement curve (Figure S6 (b)).

The properties at cryogenic temperatures were evaluated using spray-type and immersion-type methods. The size of the cryogenic chamber was 200 mm × 350 mm × 400 mm, and the cryogenic temperature of –170 °C was reached by spraying LN$_2$. After the chamber temperature reached –170 °C, the sample was held for 30 min for stabilization and then subjected to a tensile test. For the immersion-type test, a liquid nitrogen tank (310 mm × 230 mm × 35 mm) was used to create a cryogenic environment of –196 °C. At all times, only 6 lap-shear samples were placed in the liquid nitrogen tank to maintain the number per unit area. Each lap-shear sample was immersed in liquid nitrogen for 30 min and then subjected to shear testing at 23 °C.

The morphology of the PU adhesives was investigated through field emission scanning electron microscopy (FE-SEM; SUPRA 55VP, Carl Zeiss, Germany). The specimen for FE-SEM observation was immersed in liquid nitrogen and then subjected to impact to observe the fracture surface. The cut surface of a specimen was also observed after soaking in acetone for 24 h. The specimen for transmission electron microscopy (TEM) was prepared as follows. A 0.5 wt% RuO$_4$ aqueous solution was dropped on the specimen and stained for 3 h at 23 °C, and an ultrathin cross-section (25 nm to 500 nm in thickness) was prepared through cryogenic microdissection (EM FC7, Leica, Germany). The specimens were examined using a scanning TEM (STEM; Crossbeam 550, Carl Zeiss, Germany) with an acceleration voltage of 25 kV and cryo TEM (EF-TEM; Talos L120C, FEI, Czech). In cryo TEM analysis, stained cross sections were rapidly frozen, and images were captured as an electron beam emitted at a high voltage (120 kV) passed through the specimens [54]. Notably, RuO$_4$ provided a contrast between the hard and soft domains of the PU adhesive, giving the hard regions a dark appearance in TEM images [54–58].

3. Results and discussion

3.1. Characterisation of the prepolymer structure

The urethane reaction between PTMEG (a soft segment) and 4,4-MDI (disocyanate, a component of the hard segment) produced a prepolymer with isocyanates at the ends of the linear chain. PDMS diol with a short chain was employed as the chain extender at a constant molar fraction relative to PTMEG. The prepolymer synthesis process is illustrated in Scheme 1(b). The chemical structure of the synthesized prepolymer was confirmed using $^1$H and $^{29}$Si NMR (Figure S1 and Figure S2) [43,59–62].

The characteristics of the synthesized prepolymer, obtained through GPC and DSC, are summarized in Table S1. Fig. 1(a) shows the FT-IR spectra of the BM, 0.1 BM, 0.2 BM, 0.3 BM prepolymer. The NCO (2260 cm$^{-1}$) band was observed in all prepolymer samples, while the OH (3,465 cm$^{-1}$) band disappeared. For the 0.3 BM prepolymer, the stretching vibration peaks of Si-CH$_3$ and Si-O-Si appeared at approximately 2961 cm$^{-1}$ and 1257 cm$^{-1}$, respectively, consistent with the band positions of the PDMS diol.
The effect of the chemical structure of the silane-containing prepolymer on the formation of hydrogen bonds was investigated (Fig. 1(b)). Hydrogen bonds were formed through the interaction between the N-H group (proton donor) and the C=O group (proton acceptor), as shown in Scheme 1. In Figure S1(a), the stretching vibrations of the C=O groups in all prepolymers appeared at 1,711 cm\(^{-1}\) and 1,729 cm\(^{-1}\), attributed to the formation of regular hydrogen bonds. Similarly, the N-H group exhibited free vibrations at 3,400 cm\(^{-1}\), and the peak shifted to 3,300 cm\(^{-1}\) due to the formation of hydrogen bonds (Figure S1(b)). For all prepolymers, the DPS increased as the molar fraction of the silane group increased. Thus, the HI gradually increased, confirming the role of silane as a chain extender. From BM to 0.3 BM, more urethane bonds formed in the main chain of the prepolymer, increasing the DPS of C=O, thereby increasing the HI [52,63].

3.2. Characterization of the PU adhesives

In the PU structure, the main component, polyol, formed the soft domain, and the strong intermolecular hydrogen bonds led to ordered or disordered hard domains [64-66]. These hydrogen bonds served as physical cross-linking sites with chain entanglements and phase separation [67]. This configuration yielded a linear two-component PU with excellent adhesion and mechanical properties [68-71]. In each prepolymer, the ratio between the soft and hard segments depended on the molar fraction of the PDMS diol as the chain extender (Scheme 1). Thus, changing the molar ratio of PDMS could modulate the degree of physical cross-linking and the elasticity of PU.

In this study, a two-component PU adhesive was produced by mixing a polyol resin with an OH end group and a prepolymer with an NCO end group at a certain equivalence ratio (NCO index = 1.1). After curing, the mixtures became transparent specimens (Table S1) [72].

The ATR FT-IR spectra of PU specimens at different curing times and temperatures are shown in Fig. 2(a) and (b). Hydroxyl (–OH) band and isocyanate (–NCO) bands were observed at 3,465 cm\(^{-1}\) and 2,260 cm\(^{-1}\), respectively. Over time, the NCO band diminished owing to the formation of urethane bonds, and the absorbances of the N-H (3,293 cm\(^{-1}\)) and C=O functional group bands (1,728 cm\(^{-1}\)) increased. The conversion was based on the stretching vibration band of the highly variable isocyanate group (NCO, 2,260 cm\(^{-1}\)) and the band of the ether group (C-O-C, 1,101 cm\(^{-1}\)) as reference peaks. Fig. 2(c) shows the conversion of the PU adhesives.
determined based on the Beer–Lambert equation.

The microphase separation in the PU adhesives was investigated using FT-IR. Figure S3 shows the calculated DPS$_{CO}$, DPS$_{N-H}$, and HI values. The microphase separation in the PU adhesives was investigated using FT-IR. Figure S4 shows the calculated DPS$_{CO}$, DPS$_{N-H}$, and HI values. In polyurethane, H-bonding, which is a hydrogen bond between C = O and N-H of the urethane group, occurs due to intermolecular forces. Although the content of the hydrogen-bonded N-H band was constant, DPS$_{N-H}$ slightly decreased as free N-H increased. Ultimately, this C = O band is divided into three categories: A free C = O band that does not participate in hydrogen bonding (1,729 cm$^{-1}$), a C = O band (1,709 cm$^{-1}$) that participates in hydrogen bonding and has a disordered structure, and a band that participates in hydrogen bonding and has an ordered structure. This is the combined C = O band (1,650 cm$^{-1}$). Here, when PDMS was not contained, the C = O band was in the form of ordered H-bonding, but as the mole fraction of PDMS increased, the ordered C = O band decreased, and the disordered C = O band increased. As a result, DPS$_{CO}$ and the hydrogen index increased. This shows that the ordered structure of the hard domain changed due to the addition of the bulky PDMS group, increasing the intermolecular bond of the hard domain (Scheme 2) [51–53].

DSC data showed that the PU adhesives displayed only one glass transition in the second scan, with no melting temperature observed. (Figure S5) Adding PDMS to the prepolymer increased the $T_g$ of the resulting material. Thus, a thermoplastic PU adhesive with a linear structure was prepared only through diisocyanate, exhibiting strong internal interactions attributable solely to its physical cross-linking structure. The viscoelastic properties of PU adhesives were examined using small vibration deformations [73]. The PU adhesive combined with the prepolymer containing higher PDMS content exhibited a higher storage modulus. Additionally, the $T_g$ at the peak of tan delta ($T_\tan$) also increased. At temperatures above the glass transition (rubbery plateau region), $G''$rubbery decreased as the PDMS molar fraction increased. (Fig. 2 (e)) As the temperature increased (flow region), $G'$ rapidly decreased and crossed with the loss modulus $G''$ at a certain temperature ($G'=G''$, $T_2$). At temperatures above $T_2$, the material showed viscous behavior ($G'<G''$). This confirmed that the thermoplastic PU did not have a chemically cross-linked structure because the $T_m$ of an amorphous polymer does not exist, and no change in the transition region was observed [74,75]. Fig. 2 (f) shows that as the molar fraction of PDMS increased, both $T_1$ ($T_g$) and $T_2$ increased, and PU-BM$_{0.3}$ did not generate $T_2$ in the measurement range up to 200 °C. Therefore, by increasing the PDMS content, PU adhesives had more intermolecular interactions (physical cross-linking) without developing chemical cross-linking structures [76,77].

3.3. Adhesion performances of the PU adhesives

Tensile tests were conducted at different temperatures to investigate the adhesion performance of two-component PU adhesives with different molar fractions of PDMS. Given the crucial role of curing time in practical applications, the effect of curing time on adhesive performance at different curing temperatures was investigated (Figure S7 (a)). In the experiments, the specimen was ISO 527–2 1BA type, and the crosshead speed was 100 mm/min. After curing the pristine BM at 23 °C for 3 d, the tensile strength and elongation were 2.6 MPa and 480 %, respectively, suggesting its excellent physical properties as a flexible material. The FT-IR spectra in Fig. 2 (a) confirmed that optimal post-curing was 80 °C. Therefore, the change in physical properties over time was measured after 80 °C post-curing. The stress–strain curve showed higher tensile strengths and elongations as time increased. Consequently, the curing conditions for all adhesives were set as follows: 3 d at room temperature (23 °C) with post-curing in an oven at 80 °C for 3 h.

Fig. 3(a) shows the tensile test results at 23 °C. The stress of pristine PU-BM increased consistently in the elastic section, but its Young's modulus was higher than that of PU-BM samples with PDMS. In Fig. 3 (b), the pristine PU-BM had a high elongation of approximately 600 % without breaking, but a craze was observed as the volume of the specimen changed (Fig. 3 (d)). Likewise, PU-BM$_{0.1}$ caused crazing, but the craze length was shorter than that of PU-BM. Crazing did not appear in PU-BM$_{0.24}$ (Fig. 3 (e)). Crazing is primarily a failure mechanism of amorphous polymers and is associated with disentanglement in the polymer network at low strain rates. Compared to cracks, crazes do not occur during tensile testing below the glass transition [78–80]. PU-BM had low intermolecular forces at room temperature, which was favorable for crazing to occur inside the polymer. With the addition of PDMS, crazing decreased, and PU-BM$_{0.24}$, which had strong physical cross-linking, did not induce any crazing. PU-BM$_{0.3}$ exhibited similar tensile strength and Young’s modulus as pristine PU-BM, but its elongation was approximately six times lower.

The properties of PU adhesives in cryogenic-temperature conditions were evaluated to assess their feasibility. Liquid nitrogen was used to

![Scheme 2](https://example.com/scheme2.png)

Scheme 2. Schematic ordered and disordered hydrogen bonding of thermoplastic polyurethane adhesives.
create a cryogenic temperature environment. In a cryogenic temperature chamber, liquid nitrogen was sprayed to attain an internal temperature of \(-170\) °C, and measurements were performed after holding the specimen for 10 min for stabilization (Fig. 3 (h) and (i)). Fig. 3 (g) shows that the tensile strength and elongation of the PDMS-containing PU adhesives increased at 103 K, and the Young’s modulus decreased compared with those of the pure PU-BM adhesive. Specifically, at a temperature of \(-170\) °C, the tensile strength and elongation of the PU adhesive containing PDMS increased by approximately six times compared with that of pristine PU-BM. The high strength and elongation of PU-BM\(_{0.24}\) at cryogenic temperatures were attributed to the enhanced intramolecular interaction induced by adding PDMS. In addition, the dynamic performance of high-density hydrogen bonds could improve the cryogenic toughness of PU adhesives and suppress brittle fracture.

Lap-shear tests were conducted at various temperatures, including cryogenic temperatures. For the shear strength test, the same number of specimens per area (31 cm \(\times\) 23 cm \(\times\) 3.5 cm) were immersed in liquid nitrogen in a cryogenic holder for 30 min. The specimen was extracted and measured immediately (Fig. 4 (a)). The shear specimen, with an adhesive area of 1 in \(\times\) 0.5 in (25 mm \(\times\) 12.5 mm) and a thickness of approximately 0.9 mm (Fig. 4 (b)) was manufactured according to the ISO 4587 standard. Fig. 4 (c) and (d) show the lap-shear strength and force–displacement curves of the PU adhesive on sandblasted steel substrates. The lap-shear strength and work of debonding were
calculated using the maximum loading force and integral of the curve divided by the adhesion area, respectively (Figures S7(c)). The joints were cured at 80 °C for 3 h. Fig. 4(e) illustrates the failure modes observed in the shear test. The adhesive strength of adhesives is divided into adhesion and cohesion. Adhesion is the interaction between adherends and adhesives, and cohesion is a factor controlled by the internal forces of adhesives. If the interaction between the adherend and the adhesive is strong and the cohesion of the adhesive is weak, a mixed or cohesive failure mode occurs in which destruction occurs within the adhesive layer. However, if the chemical or physical bonding force that occurs at the interface between the adherend and the adhesive is weaker than the intermolecular bonding force inside the adhesive, an adhesive failure mode occurs. At −196 °C, PU-BM (Pristine) showed the highest shear strength value. Because its toughness is low compared to its high Young’s modulus at ultra-low temperatures (Figure S7(e)). Young’s modulus refers to the stiffness of a material, and toughness refers to the ability of a material to plastically deform without breaking. Additionally, mixed failure was observed for PU-BM (Pristine) after shear strength testing. According to the FT-IR results, the free C = O band is relatively large and PDMS is not added, so the interaction between the adherend and the adhesive at the interface is relatively stronger than the cohesion inside the adhesive, resulting in a mixed failure mode. Adhesive failure mode was observed for PU adhesives when PDMS was added. As hydrogen bonding increased with the addition of PDMS, the bonding force between molecules inside the adhesive also greatly increased, resulting in a strong cohesion effect. The shear strengths of PU adhesives containing PDMS were 12.5 MPa, 12 MPa, and 9.9 MPa, respectively, showing higher shear strengths at −30 °C compared to 5.3 MPa for pure PU adhesives. −30 °C is the temperature at which the molecular chain unwinds around Tg (by using DSC). Compared to PU-BM, which has weak hydrogen bonds, the high adhesive strength is due to the action of internal forces strengthened by the addition of PDMS. PDMS-based PU adhesive shows higher adhesive performance than pure PU adhesive at 0 °C and 23 °C. At 23 °C, PU-BM (Pristine) showed the lowest shear strength values. This is due to its high Young’s modulus and high toughness at room temperature (Figure S7(d)). Fig. 4(b) shows the effect of temperature on the force–displacement curve of pure PU-BM (solid line) and PU-BM0.1 (dashed line) containing 0.1 mol fraction of PDMS. At all temperatures except −196 °C, PU-BM0.1 has high shear strength and work of debonding (Figure S7(b)).

As a result, the PU-BMx adhesive showed excellent adhesive performance and high elongation at ultra-low temperatures. As shown in Fig. 5, the cryogenic properties of the PU-BMx adhesives were compared with those recently reported in the literature. PU-BMx adhesive has superior shear strength, high elongation, room temperature curing, non-solvent, and cryogenic resistance compared to other adhesives [19,22,23,25,26,29–31].

3.4. Morphology of the PU adhesives

FE-SEM was used to examine the fracture surfaces of PU adhesive specimens under various conditions. The fractured cross-section of the PU adhesive was observed after immersion in liquid nitrogen. (Fig. 6(a) and (d)). When the pristine PU-BM was frozen-fractured, a river pattern of brittle fracture was observed at low magnification. At high magnification (Figure S8), the fracture surface consisted of parallel linear striated bands. However, PU-BM0.3 showed a similar cleavage pattern at the impact point during low-temperature measurement. A uniform and dense structure was observed at high magnification, similar to that of a cross-linked structure [52,81–83]. The fully cured PU adhesive was exposed to acetone for 24 h, dried, and the fracture surface was observed (Fig. 6(b) and (e)). PU-BM contained soluble and non-soluble parts in acetone, and the non-soluble part was assessed through electron dispersive spectroscopy (EDS) to confirm the presence of C and O (Fig. 6(c)). In contrast, PU-BM0.3 maintained its shape without dissolved parts even after etching with acetone, and the presence of Si was confirmed (Fig. 6(f) and (g)).

PU adhesives possess strong toughness and mechanical strength because they are phase-separated into hard and soft domains. To distinguish the two domains under a TEM, RuO4 was used as a dye to stain the specimen. RuO4 reacts preferably with microdomains rich in hard segments [67,84–87]. Therefore, the light regions in the TEM images were composed of soft segments, and the dark regions corresponded to hard segments. The distribution of the domains depended on the location and sequence lengths of the hard segments [88–90].

STEM and cryo-TEM were employed to observe the domain shape in the PU adhesive at room temperature (23 °C) or −196 °C, respectively. Figure S10 shows the STEM images of PU adhesives unstained and stained with RuO4 at 23 °C. In the case of unstained specimens, no domains were identified. However, in the case of the RuO4-stained specimens, a dark spherical area was observed. In the STEM image of PU-BM, the dark spheres were widely distributed with a small size (approximately 200 nm). As the molar fraction of PDMS increased, the size of the dark spheres gradually increased. In particular, the diameter of the dark area in PU-BM0.3 was about 3 μm, showing a low distribution density [91].

For the cryo-TEM images captured at −196 °C, the distribution density was almost similar to the SEM image at 23 °C, and the diameter of the dark region increased with increasing PDMS content (Fig. 7). The PU-BM0.3 specimen showed the largest domain size. The TEM images represent the change in the hard domain area due to the introduction of PDMS, which had a bulky size of the prepolymer constituting the hard segment. The pristine PU-BM without PDMS was a mixture of hard and soft domain phases. Whereas, PU adhesives containing PDMS had completely separated hard and soft domains [85,92–94].

4. Conclusions

Recently, adhesives with excellent adhesion performance for cryogenic temperatures have been researched in various application fields such as aerospace, transportation, superconductors, and medicine [95–97]. This study successfully engineered a solvent-free, two-component PU adhesive formulation and evaluated the excellent adhesion properties under cryogenic conditions. The introduction of bulky polydimethylsiloxane (PDMS) diox into the prepolymer significantly strengthened hydrogen bonding in the hard segment, improving the physical properties of the PU adhesives. PU adhesives incorporated with PDMS exhibited notable tensile strength, elongation, and shear strength, particularly at cryogenic temperatures. Microscopic analysis confirmed that increasing the PDMS content enlarged the hard domain area and strengthened the physical cross-linking. Consequently, the introduction of physical cross-linking via alterations in the hard domain region led to outstanding adhesive performance under cryogenic conditions.
CRediT authorship contribution statement


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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2024.113152.

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