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Research article

Low-temperature supramolecular adhesives based on hyperbranched polyester

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Abstract. Adhesives have been widely applied in various fields. However, most industrial adhesives contain organic solvents, which are toxic and difficult to clean after use. Importantly, most adhesives are used in a relatively small temperature range (0–50 °C), which is due to the fragmentation of the morphology and properties of supramolecular polymer gels at low temperatures. Most of the supramolecular adhesives need to be heated during the bonding process, which cannot meet the requirements of low-temperature adhesion in daily life and industry. In this study, based on the concept of using deep eutectic solvents (DESs) as a platform, cyclodextrin (β-CD) and carboxyl terminated hyperbranched polyester (DCHP) were used to prepare solvent-free supramolecular polymer gel (CD-DCHP), which was non-toxic and easy to clean. Due to the joint action of deep eutectic solvent and supramolecular polymer structure, CD-DCHP showed excellent mechanical properties, super strong adhesion (up to 4.55 MPa on glass surface), and excellent low-temperature performance (up to 1.64 MPa at –60 °C). This supramolecular polymer gel also showed excellent tolerance to acids, alkalis, and various organic solvents. It greatly expanded the application of DES and provided a new approach to the development of supramolecular adhesives.

Keywords: *supramolecular adhesives, deep eutectic solvents, supramolecular polymerization, self-assembly*

1. Introduction

Adhesives are indispensable to industry, agriculture, transportation, medical treatment, national defense, and people's daily lives [1]. At present, industrial adhesives have completely replaced natural adhesives, but most of them are solvent-based, which is toxic and difficult to clean. With the development of supramolecular self-assembly, supramolecular polymer adhesives have received increasing attention [2]. The supramolecular polymer can be formed by the self-assembly of the molecular structural units through non-covalent interactions [3]. The rich supramolecular structures endow the materials with reversibility, adaptability, self-healing, and bonding functions, all of which may be attributed to non-covalent interactions [4], including hydrogen bond interaction [5, 6], metal coordination [7, 8], hydrophobic interaction [9], van der Waals force [10, 11], electrostatic interaction [12, 13] and π-π interaction [14, 15]. Supermolecular polymers have the advantage of easily changing the topological structure by introducing dynamic non-covalent interactions [16]. Traditional adhesives can only stick to wooden boards, glass, and other common substrates but are difficult to adhere to plastics (polyethylene, polytetrafluoroethylene, *etc*.) and cannot be bonded for a long time [17].

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The polymer structure in modern adhesives was crucial for achieving the adhesion effect [18], and compared with traditional adhesives, supramolecular polymer adhesives have particularly outstanding reversibility and low-temperature bonding ability.

Cyclodextrin (CD) is a naturally occurring macromolecule containing cyclic glucosyl repeating units [19]. The most studied α-, β-, and γ-CDs contain 6, 7, and 8 glucose molecules [20] respectively. The cavity of CD is hydrophobic, which can form supramolecular polymer gel through non-covalent hydrogen bonding or electrostatic interactions without affecting the biological, chemical, and physical properties [21, 22]. CDs have been widely studied in recent years. Fiorica *et al*. [23] reported the synthesis and application of CD-coated metal complexes, revealing the reversible hydrogen bonding interaction. Wu *et al*. [24] reported β-CD as a mixed carrier of smart drugs. Supramolecular polymer gel based on the CD-acid group is a kind of multifunctional material, and with the application of deep co-solvents as platforms, it has attracted extensive attention.

In this study, β-CD as hydrogen bond donor and carboxyl-ended hyperbranched polyester (DCHP) as hydrogen bond acceptor were mixed in proportion to prepare the supramolecular polymer gel (CD-DCHP) through the intermolecular and intramolecular hydrogen bonding [19]. Specifically, CD-DCHP is a supramolecular polymer gel formed by crosslinking various physical interactions, and its main driving force is the hydrogen bond interaction between CD and DCHP [25–27]. The supramolecular polymer gel based on the CD-hyperbranched polyester is a multifunctional material, so CD-DCHP is a kind of supramolecular adhesive with great development space [28].

2. Experimental sections

2.1. Materials

β-cyclodextrin (β-CD) was purchased from Meryer Chemical Technology Co., Ltd (Shanghai, China) and used as received. Carboxyl-ended hyperbranched polyester (DCHP-18) was prepared according to the procedure in the literature [29]. The chemical structures of β-CD and DCHP-18 are shown in Figures 1a and 1b, respectively.

2.2. Instruments and characterization

Fourier transform infrared spectra (FT-IR) were collected by a Vertex 470 infrared spectrometer (Bruker Company, Germany). Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 F3 thermogravimetric analyzer (NETCHI Instrument Manufacturing Company, Germany) at a heating rate of 10 °C/min from 30 to 790 °C. The nitrogen flow rate was 20 ml/min, and the amount of sample was 10 mg. Differential scanning calorimetry (DSC) measurements were carried out using NETZSCH TG 209 F3 thermogravimetric analyzer (NETCHI Instrument Manufacturing Company, Germany), with a nitrogen flow of 20 ml/min, and a heating rate of 10 °C/min from –80 to 80 °C. X-ray diffraction (XRD) spectra were collected on a Bruker-D8 X-ray diffractometer (Bruker company, Germany). Rheology measurements were performed on a DHR-1 rotary rheometer (TA Instrument Company, USA) using a 40 mm parallel laminator model 110626 Peltier steel plate at a gap of 1 mm. Scanning electron microscopy (SEM) images were collected on a SU8010 electron microscope (Hitachi Company, Japan). The adhesion strength was tested on a 5966 universal testing machine (INSTRON Company, USA). Nuclear magnetic resonance (NMR) spectra were collected on an AVANCE III 400 MHz NMR instrument (Bruker Company, Germany).

2.3. Preparation of supramolecular polymer gel

Preparation of CD-DCHP-*x* (*x*: Molar ratio of β-CD to DCHP-18): In a typical procedure, β-CD (1.5 mmol, 1.7017 g) and DCHP-18 (1.5 mmol, 1.8150 g) were added into a 100 ml beaker, then 80 ml ultrapure water was added. The mixture was stirred at 25 °C for 30 min and then dried at 80 °C for 10 h. During heating, a transition from solid mixture to viscous liquid was observed, and the supramolecular polymer gel could be obtained by cold sweat at room temperature. A series of supramolecular polymer gels with different molar ratios of β-CD to DCHP-18 was prepared using a similar method, as summarized in Table 1. No reprocessing or further

Table 1. The proportion of each component of CD-DCHP-*x*.

Supramolecular polymer gel	Moles [mmol]		Molar ratio of DCHP-18/β-CD (*x*)
	β-CD	DCHP-18	
CD-DCHP-0.5	3.0	1.5	0.5
CD-DCHP-1	1.5	1.5	1.0
CD-DCHP-1.5	2.0	3.0	1.5
CD-DCHP-2	2.0	4.0	2.0
CD-DCHP-3	2.0	6.0	3.0

treatments are needed before applying these polymer gels for adhesion tests.

2.4. Preparation of bonded sample bars

Take glass substrate as an example. The supramolecular polymer gel was evenly coated on a piece of glass and then covered with another glass plate and pressed for 10 min, with an adhesion area of 6.25 cm^2. The pair of adhered glass sheets were heated at 80 °C for 60 min and then cooled to room temperature for tensile tests.

3. Results and discussion

The mixtures of CD and DCHP-18 were used to synthesize deep eutectic supramolecular polymers (DESPs) by simple heating [30]. An irreversible transformation from the solid mixture (CD and DCHP-18) to high viscosity supramolecular polymer gel was observed in the process (Figure 1), which was a good indication that supramolecular polymerization had taken place between β-CD and DCHP-18. Flexible and viscous fibers can be easily extracted from the viscous gel (Figure 1d) [31]. The hydrogen bonding formed in supramolecular polymers not only affects the aggregation but also affects the morphology of supramolecular polymers. Moreover, the infrared spectra of the supramolecular polymer gel fully match the standard of deep eutectic solvent [18, 25]. The FT-IR spectra of CD, DCHP, and CD-DCHP are shown in Figure 2a. In Figure 2a, the characteristic peaks of β-CD appeared at 3321, 2932, and 1030 cm^{-1}, corresponding to –OH, C–H, and C–O stretching vibrations, respectively [21]. The characteristic peaks of DCHP appeared at 1172, 1699, 1750, and 3292 cm^{-1}, which corresponded to the stretching vibrations of C–O–C, C=C, C=O and –OH groups, respectively [32]. In the spectrum of CD-DCHP-1, the vibration of C=O shifted to 1716 cm^{-1}, the intensity of the characteristic C–O–C peak decreased somewhat, and new peaks due to the formation of CD-DCHP-1 appeared at 2947 and 1032 cm^{-1}. Compared with β-CD, the absorption of the –OH group

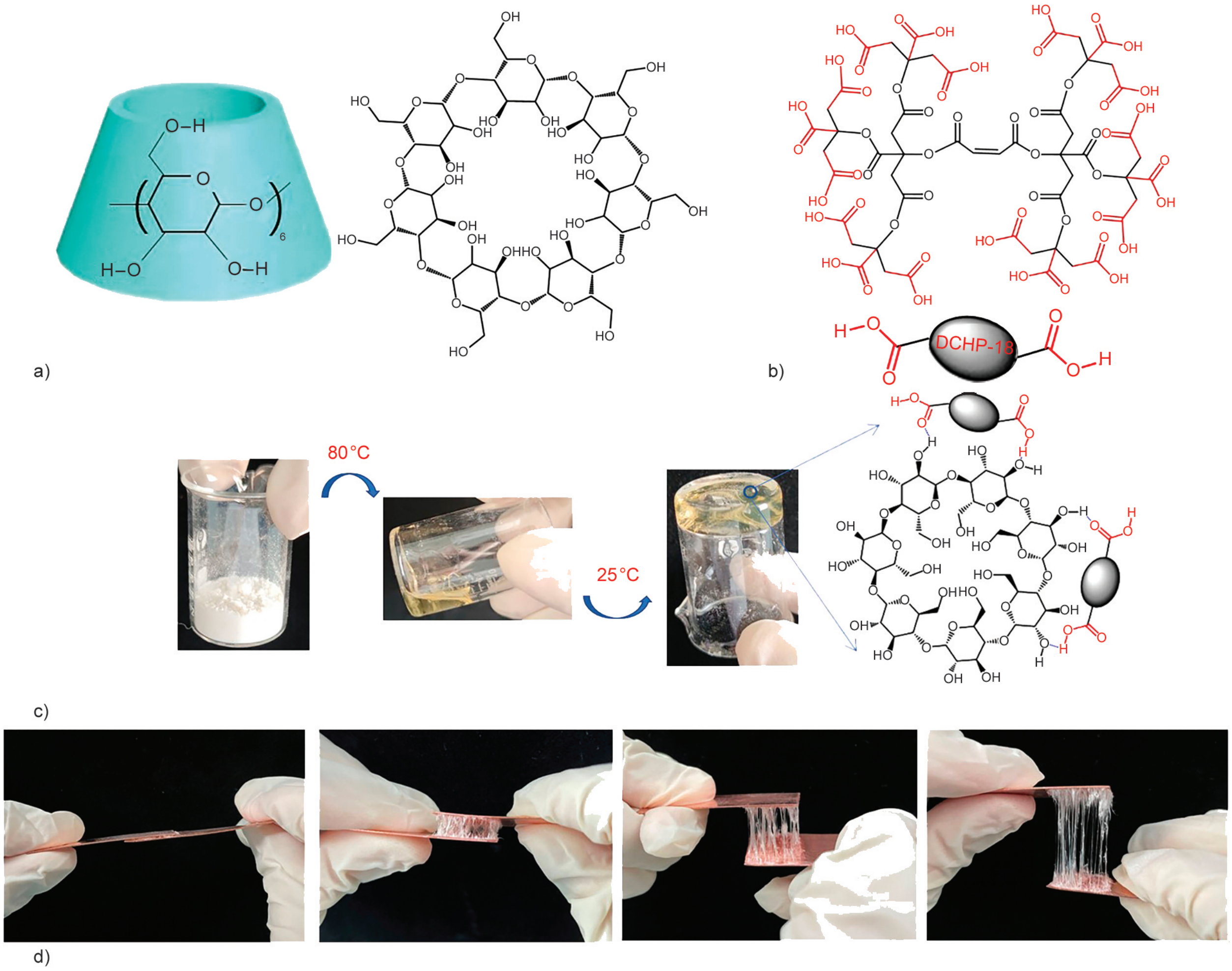

Figure 1. Chemical structures of a) CDs and b) DCHP-18, c) preparation of supramolecular polymer gel, d) the fibers drawn from CD-DCHP.

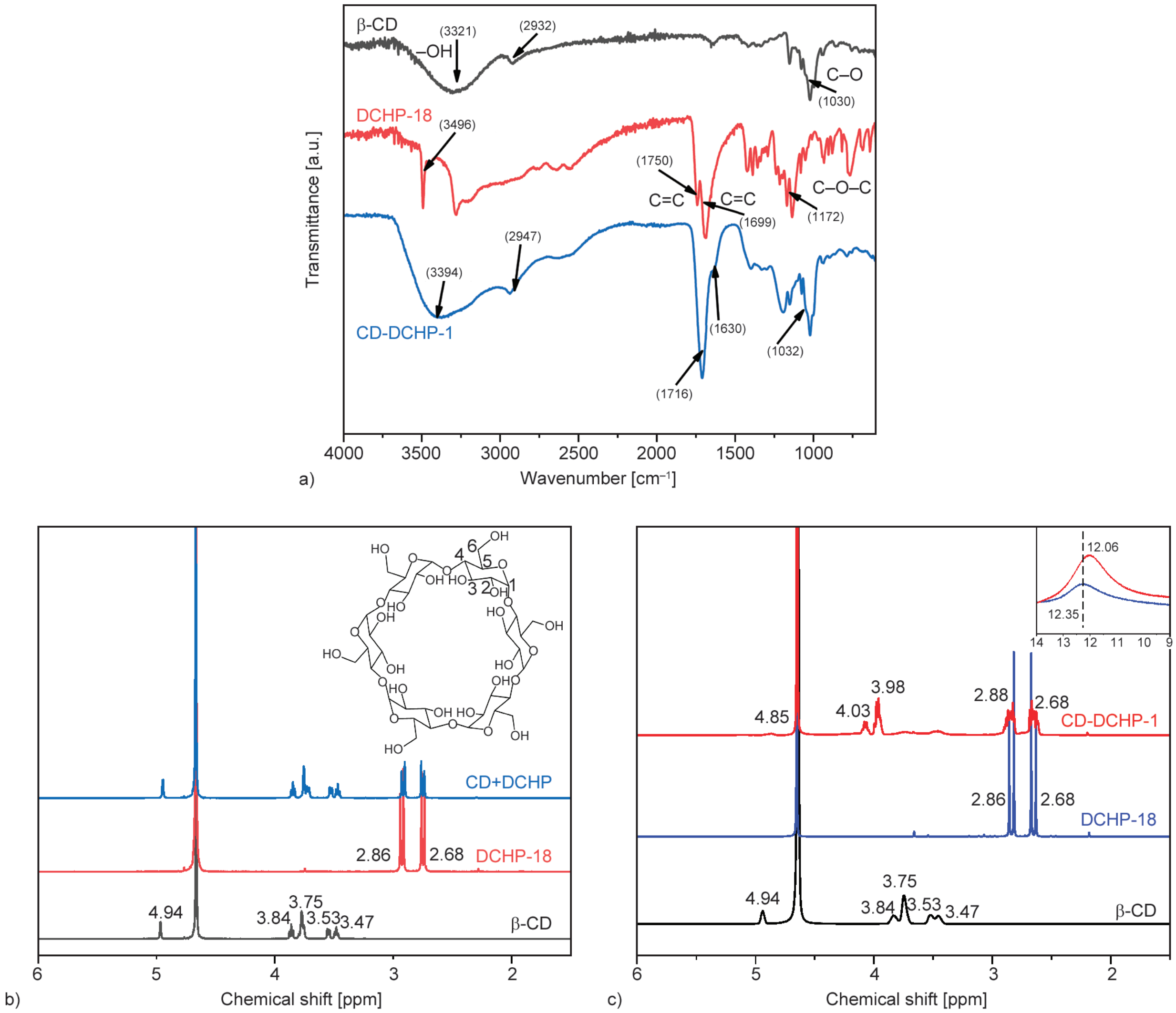

Figure 2. a) FT-IR spectra of CD, DCHP-18, and CD-DCHP-1, b) ^{1}H-NMR comparison of CD, DCHP-18, and CD+DCHP, and c) ^{1}H-NMR spectra of CD, DCHP-18, and CD-DCHP-1, insert: chemical shift at 14–9 ppm.

of CD-DCHP-1 (3394 cm^{-1}) was shifted and intensified as a result of the formation of hydrogen bonding between the C=O of DCHP-18 and the –OH of β-CD. [33–36]. The IR spectra of CD-DCHP-1 were consistent with the formation of typical deep eutectic solvents [25].

CD-DCHP-1, β-CD, DCHP-18, and the heated mixture of β-CD and DCHP-18 (named CD+DCHP) were tested by ^{1}H-NMR (Figures 2b, 2c). As can be seen from Figure 2b, the chemical shifts of –OH at positions 2, 3, 4, and 6 in β-CD were 3.53, 3.84, 3.47, and 3.75 ppm, respectively [37]. The chemical shift of –COOH in DCHP-18 was 12.35 [32], and compared with the ^{1}H-NMR spectra of β-CD and DCHP-18, the characteristic peaks of simple mixture CD+DCHP showed no change, suggesting that there was no hydrogen bonding interaction. On the other hand, the chemical shifts of –OH at positions 3 and 6 of β-CD in CD-DCHP-1 shifted downfield from 3.84 and 3.75 ppm to 4.03 and 3.98 ppm (Figure 2c), respectively, and the hydroxyl peaks at positions 2 and 4 gradually disappeared. Meanwhile, the chemical shift of –COOH in DCHP-18 shifted from 12.23 to 12.31 ppm (insert in Figure 2c). All these proved that –OH in β-CD and –COOH in DCHP-18 have formed hydrogen bonding. The ^{1}H-NMR results also provided evidence that CD-DCHP-1 was a hydrogen-bonded supramolecular complex [38].

The solid-state structure of CD-DCHP-1 was investigated by XRD and shown in Figure 3a. There was a wide diffraction peak centered around 20°, which was typical of an amorphous structure. This was because CD-DCHP-1 formed hydrogen bonds during the synthesis, which inhibited the crystallization of the chain segments [39]. Combining the results of the ^{1}H-NMR spectrum of CD-DCHP-1, it is concluded

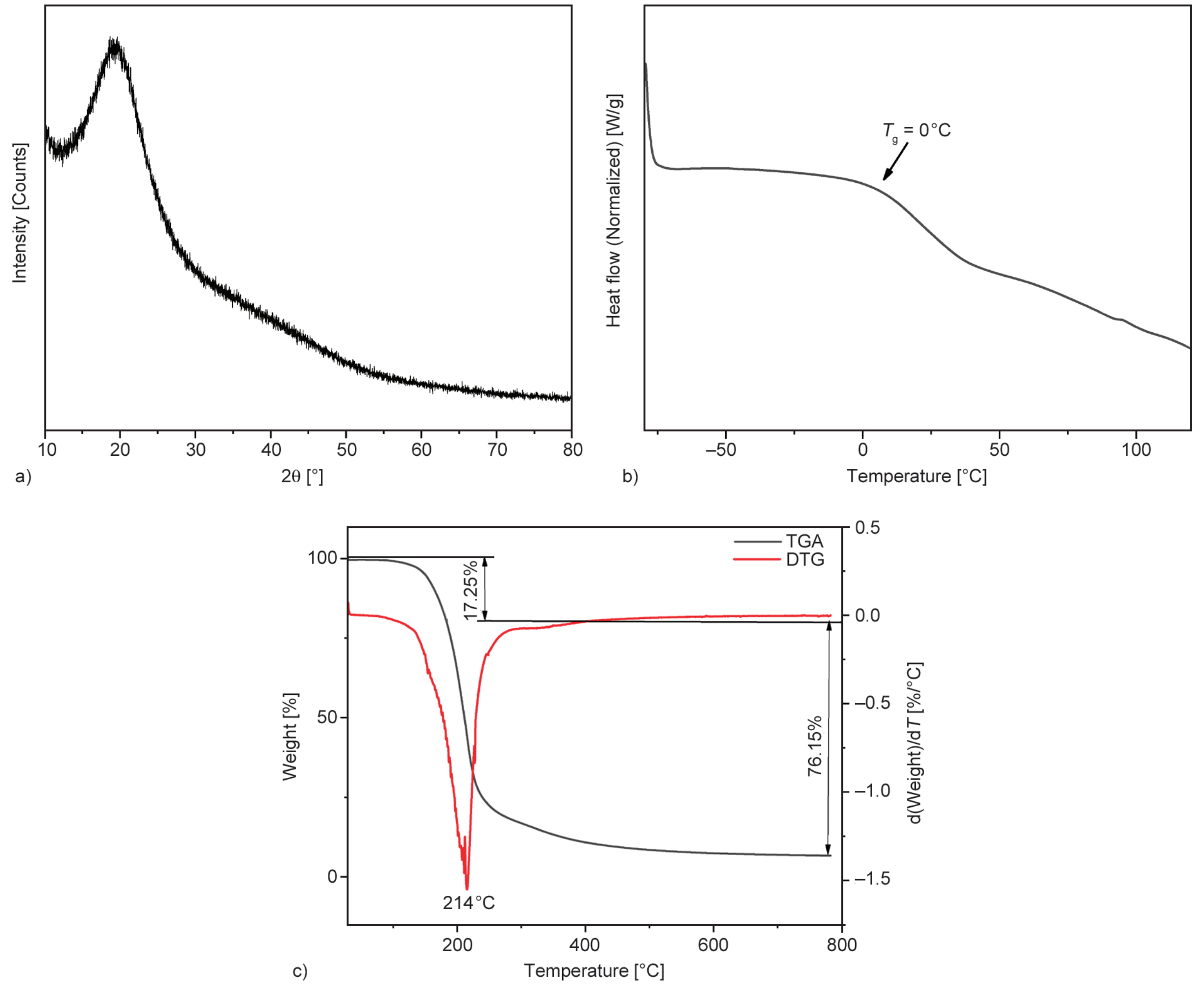

Figure 3. a) XRD pattern of CD-DCHP-1, b) DSC, and c) TGA characterization of CD-DCHP-1.

that there is a hydrogen bond interaction between –OH in β-CD and –COOH in DCHP-18.

The thermal stability of CD-DCHP-1 was tested by DSC and TGA. As shown in Figure 3b, the glass transition temperature of CD-DCHP-1 was about 0 °C, which was lower than room temperature [40]. The TGA curve showed that the gel began to lose weight at about 100 °C (Figure 3c), owing to the loss of hydrophilic binding water. The initial and maximum degradation temperatures were 135 and 214 °C, respectively, and the physical and chemical properties of the gel remained the same below 135 °C, indicating high thermal stability [40, 41]. It showed that the CD-DCHP-1 was not only suitable for general bonding applications but also suitable for application at low temperatures.

The rheology of CD-DCHP-*x* was also studied, and the mechanical properties of supramolecular adhesive were quantitatively evaluated by a dynamic frequency scanning test. Under the condition of a fixed strain of 0.1%, an angular frequency increment of 5 rad·s^{-1} between 1 and 100 rad·s^{-1}, the storage modulus (*G′* of different supramolecular adhesives CD-DCHP-0.5, CD-DCHP-1, CD-DCHP-2, and CD-DCHP-3 were measured and shown in Figure 4b. When the molar ratio of β-CD to DCHP-18 is 1:1, the modulus was at a maximum due to the fact that the molar ratio of –OH to –COOH was also 1:1, thus forming a dense hydrogen bonding network. As shown in Figure 4a, there was no intersection point between *G′* and (*G″*) with the increase of frequency, and the storage modulus (*G′*) was always smaller than the loss modulus (*G″*), suggesting that CD-DCHP-*x* had always been a viscoelastic gel, and had no tendency to change into solid fluid [40, 42].

Dynamic temperature scanning on different CD-DCHP-*x* samples was performed, with the results presented in Figure 4b. The viscosity gradually decreased with the increase in temperature due to the breaking of hydrogen bonds, and the fluidity of CD-DCHP-*x* increased. However, when the temperature decreased, hydrogen bonds would be formed

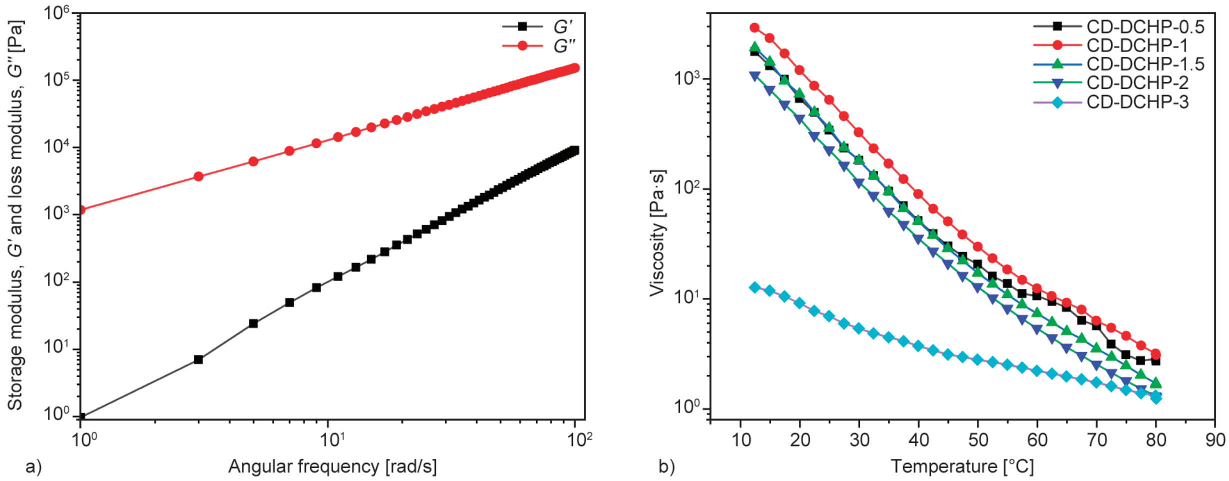

Figure 4. a) Storage modulus (G') and loss modulus (G'') values of CD-DCHP-1 on frequency sweep at 25 °C, b) effects of temperature on viscosity of CD-DCHP-*x*.

again, giving the supramolecular gels adhesive force, as proved in the subsequent reuse experiments. This showed that supramolecular adhesive was a kind of physical gel constructed by intermolecular hydrogen bonding interaction, so when the external environment changed or external forces acted on, it would affect the adhesive strength.

The XPS spectra of β-CD, DCHP-18, and CD-DCHP-1 were shown in Figure 5a, all of which displayed carbon and oxygen peaks. Narrow scans for C 1s and O 1s were performed at 285–298 eV and 520–545 eV and shown in Figures 5b, 5c, respectively. Compared with β-CD and DCHP-18, the binding energy of C 1s increased, and that of O 1s decreased in the spectrum of CD-DCHP-1, also an indication of the formation of hydrogen bonds between β-CD and DCHP-1.

The C 1s spectrum of β-CD was deconvoluted into three peaks (Figure 5d): 283.69 eV belonged to C–H, 285.36 eV belonged to C-C, and 286.76 eV belonged to C–OH and C–O–C. The C 1s spectrum of DCHP-18 was divided into five peaks (Figure 5e): 284.09 eV belonged to C–C and C–H, 285.92 eV belonged to C=C, and 288.32 eV belonged to C–OH and O–C=O [41]. The deconvolution of C 1s subpeak of CD-DCHP-1 was also performed (Figure 5f), and five peaks of 283.85, 285.78, 287.80, 288.4, and 289.1 eV were obtained. The binding energy of C–H and C–C increased and overlapped at 283.85 eV. The peak at 285.78 eV was attributed to C=C, 288.4 eV to C=O, 289.1 eV to O–C=O, and the new peak at 287.80 eV was attributed to C=O···O–H after hydrogen bonding interaction.

O 1s spectra of β-CD, DCHP-18, and CD-DCHP-1 were deconvoluted and shown in Figure 5g–5i. The 531.49 and 532.12 eV peaks of O 1s were attributed to C–O–C and C–OH of β-CD, respectively. The 531.39, 532.40, and 533.22 eV peaks were attributed to C–O–C, C=O, and O–C=O of DCHP-18, respectively. The O 1s of CD-DCHP-1 have been divided into five peaks, 530.59, 531.19, 532.65, and 533.37 eV, which were attributed to C–OH, C–O–C, C=O, and O–C=O respectively, while the new peak at 531.83 eV was attributed to C=O···O-H, also proving that there existed hydrogen bonding interaction between β-CD and DCHP-18.

The CD-DCHP-*x* showed superior adhesion strength on the surface of various materials. As can be seen from Figure 6, it can easily adhere to wood, polytetrafluoroethylene (PTFE), paper copper, carnelian, rubber, aluminum, copper, iron, glass, and silicone [30]. The adhesion properties were carefully studied from the aspects of polymerization behavior and macroscopic properties. As can be seen from Figure 7a, it can be easily bonded on different substrates. CD-DCHP-*x* was firstly coated on the surface of the substrate at 80 °C for 1 hour; then, a new substrate was covered. After pressing for 30 min, the two pieces of substrates were adhered together, followed by cooling to room temperature (Figure 7a) [42].

The bound glass and steel sheets did break apart or misalign when attached with a weight of 10 kg (the adhesion area is 6.25 cm^2, Figures 7a, 7b), clearly demonstrating strong and stable adhesion. The CD-DCHP-1 bonded copper sheet was less strong but could also hold up to 6 kg of weight (Figure 7c) [17].

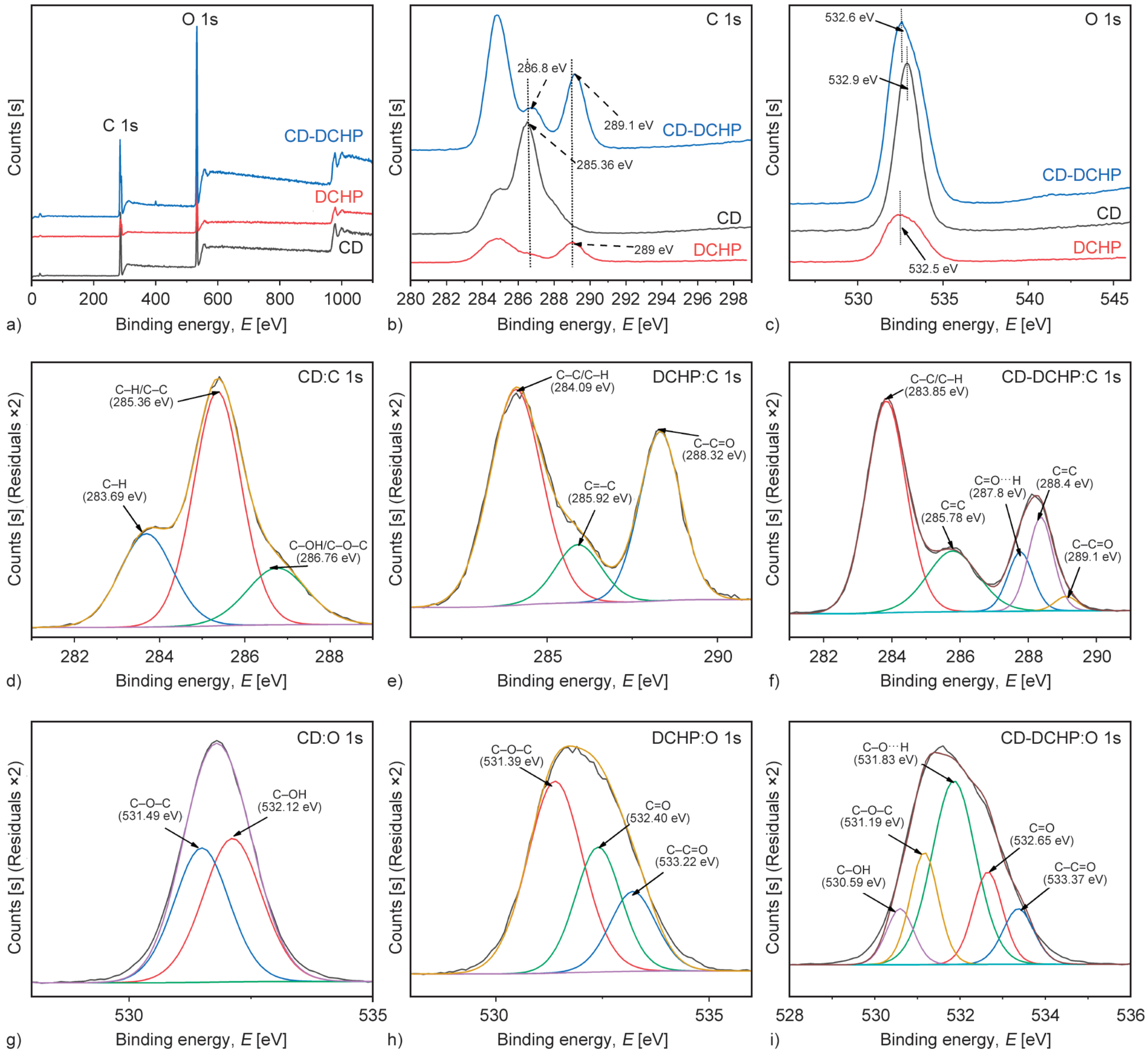

Figure 5. XPS full spectrum (a), C 1s (b, d–f) and O 1s (c, g–i) XPS spectrum of β-CD, DCHP-18, and CD-DCHP-1.

The CD-DCHP-*x* adhesives with various CD to DCHP-18 ratios were applied for the adhesion tests at 25 °C. The adhesive strength of CD-DCHP-*x* (Figure 8a) on glass increased first and decreased afterward as the molar ratio of β-CD to DCHP-18 increased [17]. The adhesive strengths of CD-DCHP-0.5, CD-DCHP-1, CD-DCHP-1.5, CD-DCHP-2, and CD-DCHP-3 were 2.52±0.23, 4.02±0.08, 2.78±0.24, 1.98±0.43, and 1.47±0.12 MPa, respectively, with the maximum fount at a 1:1 ratio. When the molar ratio of β-CD to DCHP-18 was 1:1, the ratio of –OH to –COOH was also 1:1, which was conducive to forming a dense hydrogen bond network. The shear adhesion strength of CD-DCHP-1 to different types of substrates was measured, as can be seen in Figure 8b. The shear adhesion strengths of the CD-DCHP-1 for iron, steel, wood, aluminum, and glass substrates were 1.21±0.18, 1.73±0.11, 2.41±0.24, 2.48±0.21, and 4.02±0.08 MPa, respectively, demonstrating excellent adhesion property for various substrates.

Supramolecular assembly is usually sensitive to temperature. The shear tests at different temperatures showed that high temperature was not conducive to the bonding of CD-DCHP-1 on the substrate, as depicted in Figure 8c. Too low a temperature was also shown to reduce the adhesion strengths. The adhesive strength of CD-DCHP-1 (Figure 8c) on a glass plate increased first and decreased afterward as the temperature increased from –60 to 25 °C, which were 1.64±0.04 MPa at –60 °C, 1.85±0.24 MPa at –30 °C, 1.94±0.20 MPa at –20 °C, 3.13±0.22 MPa at –10 °C, 4.08±0.18 MPa at –0 °C, 4.55±0.21 MPa at 10 °C, and 4.02±0.08 MPa at 25 °C, respectively.

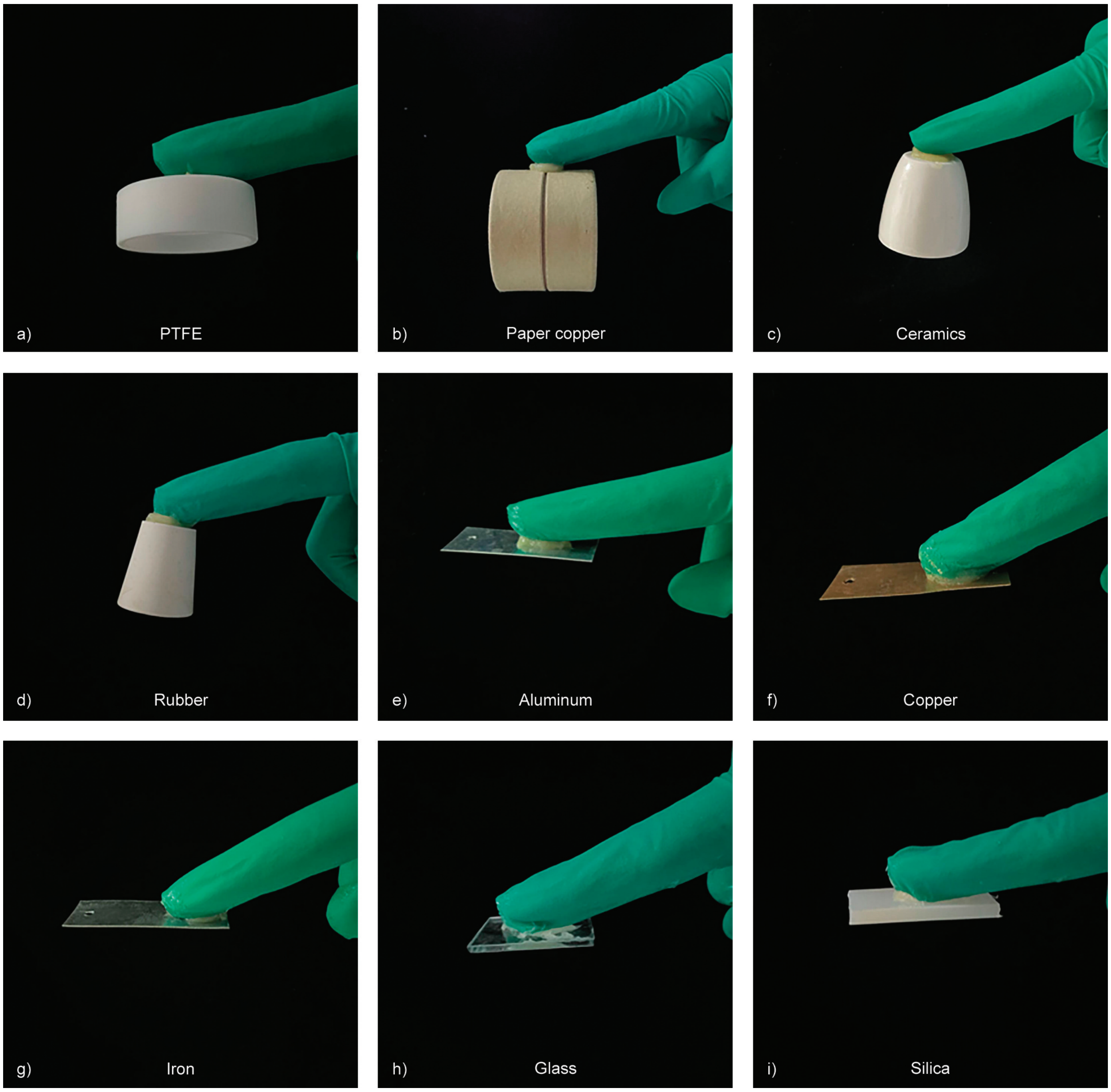

Figure 6. Schematic diagram of adhesion of CD-DCHP-1 to a) PTFE, b) paper copper, c) ceramics, d) rubber, e) aluminum, f) copper, g) iron, h) glass, and i) silica.

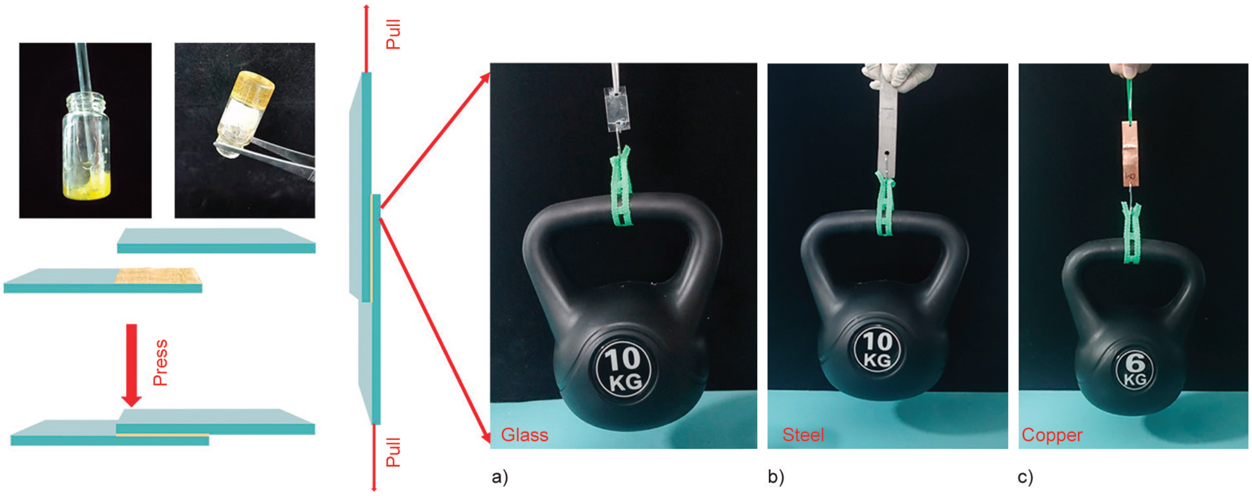

Figure 7. Adhesion experiment and adhesion properties of CD-DCHP gel to a) glass, b) steel, c) copper.

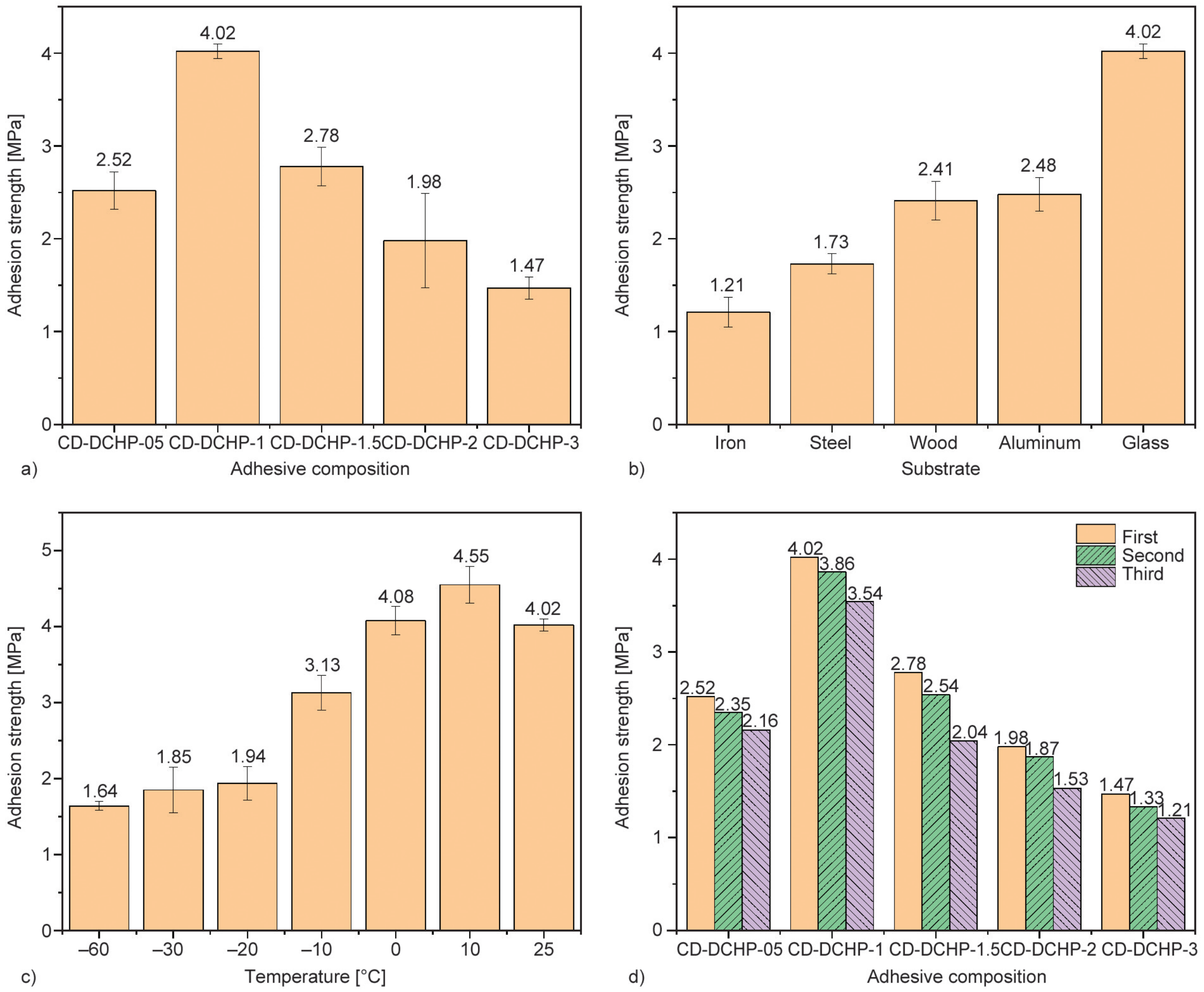

Figure 8. a) Tensile test of CD-DCHP with different proportions, b) tensile test of CD-DCHP-1 gel on different substrates, c) tensile test of CD-DCHP-1 gel on the glass surface at different temperatures, d) cyclic tensile test of different proportions of CD-DCHP on the glass plate.

The adhesion results varied with temperature in accordance with rheological measurements and macroscopic adhesion tests (Figure 4).

After three heating and cooling cycles on the steel substrate, the bonding strength of CD-DCHP-1 remained around 3.54 MPa (Figure 8d), indicating excellent reusability [40]. Although the tensile external force destroyed the hydrogen bonding, it tended to form again after cooling down and made the glass plates stick together again. However, due to the increase of plasticity after repeated heating, the bonding strength of CD-DCHP-1 decreased slightly [42], as shown in Table 2.

Figure 9 presents the adhesion tests after soaking the plates in various solvents. As can be seen from Figure 9a, the adhesive force was still maintained after soaking in liquid nitrogen (–196 °C). To test the resistance of CD-DCHP-1 to organic solvents, CD-DCHP-1 was immersed in transformer oil and *N*-octane, and a 1 kg object could be hung on the adhered glass sheet without breaking up or displacement (Figures 9b, 9c). All these indicated that CD-DCHP

Table 2. Cyclic tensile test of different proportions of CD-DCHP on the glass plate.

Number of cycles	**Adhesion strength [MPa]**				
	CD-DCHP-0.5	**CD-DCHP-1**	**CD-DCHP-1.5**	**CD-DCHP-2**	**CD-DCHP-3**
1	2.52	4.02	2.78	1.98	1.47
2	2.35	3.86	2.54	1.87	1.33
3	2.16	3.54	2.04	1.53	1.21

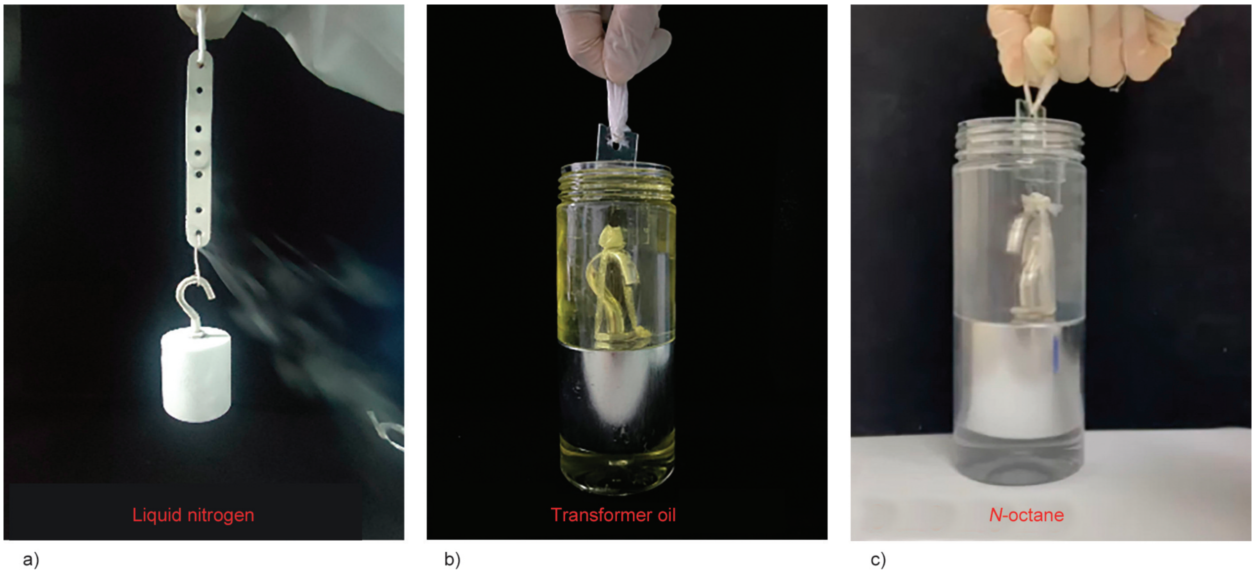

Figure 9. a) Macro bonding test of CD-DCHP-1 on steel sheet (soak in liquid nitrogen for 10 min after bonding), b) transformer oil, and c) *N*-octane of CD-DCHP-1 on the glass sheet.

could be used in some harsh environments and had good tolerance to various solvents.

4. Conclusions

In conclusion, supramolecular adhesives based on hyperbranched polyester and cyclodextrin (CD-DCHP-*x*) were constructed by hydrogen bonding interaction between β-CD and DCHP-18. A dense hydrogen bonding network was formed to provide excellent adhesions by utilizing the rich hydroxyl groups in β-CD and the carboxyl groups in DCHP-18. The successful synthesis of supramolecular adhesives was confirmed by FT-IR, ^{1}H-NMR, XRD, and XPS. Tensile tests show that the binding effect of β-CD and DCHP-18 is the best when the molar ratio of β-CD to DCHP-18 is 1:1 (CD-DCHP-1). CD-DCHP-1 also showed excellent adhesion on various substrates (iron sheet, wood sheet, aluminum sheet, glass, *etc*.), with adhesive strengths found between 1.21 and 4.55 MPa. Tensile tests of CD-DCHP-1 at different temperatures showed that the supramolecular adhesives were not only suitable for room-temperature application but also worked well at low-temperature. The adhesive strengths of CD-DCHP-1 were 1.64±0.04 MPa at –60 °C, 1.85±0.24 MPa at –30 °C, 1.94±0.20 MPa at –20 °C, 3.13±0.22 MPa at –10 °C, 4.08±0.18 MPa at –0 °C, 4.55±0.21 MPa at 10 °C, and 4.02±0.08 MPa at 25 °C, respectively. The adhesives also demonstrated excellent reusability and resistance to various organic solvents. The cyclic tensile test of CD-DCHP-1 showed that the supramolecular bond between different substrates was reversible and could be reused multiple times.

Acknowledgements

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