Supramolecular Adhesive Materials from Natural Acids and Sugars with Tough and Organic Solvent-Resistant Adhesion

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Natural adhesives have been widely replaced by industrial adhesives made from petroleum-based products. Compared with that of traditional natural adhesives, modern industrial adhesives show improved adhesion performance. However, the drawbacks of modern adhesives, including toxicity and nonbiodegradability, drive the need for new and high-performance adhesive materials from renewable and biocompatible natural feedstock. In this study, a new family of acid–sugar adhesive materials exhibiting excellent and long-term adhesion effects was developed inspired by the concept of deep eutectic solvents (DESs). The supramolecular polymerization between natural sugars and acids gave rise to both strong cohesion and adhesion properties. Moreover, high resistance to organic solvents is an advantage of acid–sugar supramolecular adhesive materials. This study not only dramatically expands the applications of DESs but also sheds light on the development of supramolecular adhesive materials as promising alternatives to polymeric adhesives.

Keywords: supramolecular adhesive materials, deep eutectic solvents, supramolecular polymerization, supramolecular adhesion, supramolecular polymers
Introduction

In ancient times, sugars and starches were frequently used as ordinary adhesives to adhere papers, textiles, leathers, and other materials. Experimental and mechanistic studies clearly demonstrated that the hydrogen bond formation between water and sugar was crucially related to the adhesion behavior.1-3 Water molecules that are buried within sugars tighten sugar molecules by hydrogen bonds, to form supramolecular polymeric networks.4,5 Supramolecular polymer structures and hydrogen bond formation give rise to the cohesive and adhesive properties.6-9 However, water can be easily removed from the sugar-water supramolecular polymeric systems during the practical adhesion process, thus leading to a significant attenuation of adhesion strength or adhesion effect.10,11

With the rapid development of artificial polymeric adhesives in the past century, natural adhesives were no longer the research focus of modern adhesives.12-16 In addition, the relatively weak adhesion capacities and the presence of water become obvious disadvantages, hindering the functionalization of sugar adhesives.17-20 Sugar adhesives were therefore unable to keep pace with the expanding practical applications of modern polymeric adhesives,21-23 even though many modern polymeric adhesives are toxic or nonbiodegradable.24,25

To overcome the drawbacks of sugar adhesives, it is necessary to develop new adhesive components other than water. In natural systems, sugars are always linked with proteins to form glycoconjugates,26,27 such as glycoproteins and proteoglycans, via the bond formation between hydroxyl groups from sugars and carboxylic groups from amino acids. Inspired by the conjugation between sugars and amino acids, natural acids have great potential to develop new adhesive materials with sugars, because the hydrogen bond formation between sugars and acids are abundant, and natural acids are nonvolatile in comparison with water.

Sugars and poly(acids) were then used to prepare adhesive materials by reacting at high temperature (178 °C).28 Such high reaction temperature not only yielded the adhesion property (the formation of high molecular weight polymers by the esterification between hydroxyl groups in sugars and carboxylic groups in acids) but also led to the caramelization of sugars and/or acids. The caramelization phenomena of adhesive materials dramatically affected the adhesion effect and became an obvious drawback of practical applications. In recent years, a large number of deep eutectic solvents (DESs) based on natural sugars and acids have been successfully designed and synthesized.29-37 DESs are bulk eutectic mixtures of two or more monomers, which act as hydrogen bond acceptors and/or donors.29-38 From the view of cross-linked polymeric supramolecular systems,39-42 in DESs, the formation of three-dimensional hydrogen bond networks leads to the occurrence of many interesting and useful features, including high viscosity.32-38 In fact, the high viscosity of sugar-acid supramolecular complexes was frequently ignored or even avoided in the wide applications of DESs.43-46 In our previous work, we developed cyclodextrin-acid supramolecular adhesives.9 However, the combination of DESs, adhesion, and supramolecular polymerization represents a new but still rarely acknowledged method to prepare supramolecular adhesives.9,38,46

Here, we report a series of acid-sugar adhesive materials that exhibit tough and long-term adhesion effects on various surfaces. Kilogram-scale and eco-friendly adhesives were prepared in an facile route. Water is replaced by natural acids in the compositions of sugar adhesive materials. The hydrogen bond formation between sugars and acids leads to the fabrication of supramolecular polymers, which dramatically improves the adhesion capacity and sustainability.4,9,39,40,41 Strong, recyclable, and long-term adhesion performance on a wide range of substrates originate from the reversible hydrogen bonding and dynamical supramolecular polymerization.42 Importantly, acid-sugar adhesive materials are highly resistant to organic solvents, and tough adhesion behavior is easily achieved in various organic solvents.

Experimental Methods

All materials and reagents were commercially obtained and used without further purification. Infrared (IR) spectra were collected on a Thermo Scientific Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA). Thermogravimetric (TGA) analysis (TGA) was carried out using a NETZSCH STA 449 F3 Jupiter (NETZSCH-GERÄTEbau GmbH, Selb, bavaria, Germany), from 20 to 400 °C at a rate of 10 °C/min in nitrogen atmosphere. Differential scanning calorimeter (DSC) measurements were carried out using a TA Q2000 (TA Instruments, New Castle, Delaware, USA), from −40 to 80 °C at a rate of 10 °C/min in nitrogen atmosphere. X-ray diffraction (XRD) data were collected on a Bruker D8 ADVANCE (Bruker, Karlsruhe, Baden-Württemberg, Germany). Rheology measurements were performed on an Anton Paar MCR 92 (Anton Paar, Graz, Steiermark, Austria). The laminator model PP15 was chosen with a diameter of 15 mm with the gap at 1 mm. Scanning electron microscopy (SEM) images were collected on a HITACHI UHR FE-SEM SU8010 (HITACHI, Tokyo, Japan). The adhesion strength measurements were performed on a HY-0580 Electronic tensile testing machine (Shanghai Heng Wing Precision Instrument, Shanghai, China). Proton nuclear magnetic resonance (1H NMR) spectra and concentration-dependent 1H NMR spectra were...
collected on a Varian Unity INOVA-400 (Varian, Palo Alto, California, USA) or Bruker-AV400 (Bruker, Karlsruhe, Baden-Württemberg, Germany). Two-dimensional correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) experiments were performed on a Bruker-AV400 MHz spectrometer (Bruker, Karlsruhe, Baden-Württemberg, Germany). Two-dimensional diffusion-ordered spectroscopy (DOSY) spectra were recorded on a Bruker-AV600 MHz spectrometer (Bruker, Karlsruhe, Baden-Württemberg, Germany). Concentration-dependent viscosity experiments were done on a Brookfield DV2TLVTJ0 Viscometer (Brookfield, Middleboro, Massachusetts, USA). Microstructure of supramolecular material’s fiber was observed under an Inverted light microscope LWD200-37T1 (Shanghai Cewei Photoelectricity Technology, Shanghai, China). Isothermal scanning calorimetric measurements were carried out on a Nano ITC (TA Instruments, New Castle, Delaware, USA).

Preparation of acid–sugar supramolecular adhesive materials

Twelve acid–sugar adhesive materials were synthesized according to reported methods. Taking preparation of citric acid–(+)-fructose supramolecular adhesive material as an example, citric acid (19.2 g, 0.1 mol) and (+)-fructose (18.0 g, 0.1 mol) were added into a 100 mL flask, and water (20 mL) was added into the flask. The mixture was stirred at 25 °C for 10 min, then the mixture was dried at 60 °C for 12 h without stirring (the flask is open). A transition from a mixture of solids to a viscous liquid was observed during the heating process. The viscous liquid was treated under vacuum for 1 h. Without further purification or isolation processes, the viscous liquid was directly used for the adhesion and other tests. The details of the preparation of acid–sugar adhesive on a large scale were described in the Supporting Information (Supporting Information Figure S1).

The adhesive coating on different surfaces (with the coating on the glass as an example)

Acid–sugar adhesive materials were coated on one glass slice which was covered by another glass slice. The adhered pair of glass slices was heated at 60 °C for 30 min and was stored under different conditions before the pull-off adhesion tests. The amount of the adhesive was kept at ca. 10 mg/cm².

Results and Discussion

Two natural acids, citric acid (C) and L-(-)-malic acid (M), were chosen to replace water. D-(-)-trehalose (T), D-(-)-fructose (F), D-(-)-glucose (G), and sucrose (S) were used to form hydrogen bond networks with natural acids (Figure 1 and Table 1). Acid–sugar adhesive materials were prepared by heating a mixture of different natural sugars and acids at 60 °C for 30 min, as a typical method to prepare DESs. Temperature-induced transitions from mixtures of nonsticky solids to highly viscous soft materials were observed (Figure 1b and Supporting Information Videos S1 and S2), indicating the occurrence of supramolecular polymerization between the sugars and acids. In constrast, individual acids or sugars were nonviscous and did not show any adhesion effect. Compared with the 1H NMR spectra of the simply mixed sugars and acids, no changes were observed in the 1H NMR spectra of deep eutectic supramolecular adhesive materials (Figure 1b and Supporting Information Figures S2–S13), which demonstrated that no esterification or etherification took place at 60 °C. The 1H NMR results also confirmed that deep eutectic supramolecular adhesives were hydrogen-bonded supramolecular complexes, which can decomplex to individual acids and sugars in D2O. As shown in concentration-dependent 1H NMR spectra (Supporting Information Figures S14–S25), it was demonstrated that when the concentrations of DESs were increased from 4 to 1200 mg/mL, no supramolecular polymerization behavior was observed. This information indicated that at the solution state, due to the

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strong solvation effect of water molecules (the interaction between water molecules and natural sugar/acid molecules), natural sugars and acids existed in a monomer-type state. Two-dimensional DOSY, NOESY, and titration experiments further confirmed these observations (Supporting Information Figures S26–S65). Concentration-dependent viscosity tests clearly showed that at the solution state, the increase of the concentration only exerted slight influence on the viscosity (Supporting Information Figures S66 and S67). However, when in a mixture of DESs and water (water content is below 25-15%), a rapidly increased viscosity was observed, indicating the formation of supramolecular polymeric structures (Supporting Information Figure S68). These observations fit the features of our previously reported supramolecular polymers with deep eutectic properties. The attenuated total reflectance IR (ATR-IR) spectra of the acid–sugar adhesive materials further confirmed the hydrogen-bonding formation (Supporting Information Figures S69 and S70). Acid–sugar supramolecular adhesive materials were amorphous and thermostable, according to their powder XRD (PXRD) patterns and TGA, respectively (Supporting Information Figures S71–S74).

As shown in Supporting Information Figures S75 and S76, supramolecular adhesive materials possessed low glass transition temperature. Dense and smooth surface morphology of the acid–sugar adhesive materials were observed by SEM (Supporting Information Figure S77). All acid–sugar adhesive materials showed high viscosities (1.8 × 10⁴ to 5.9 × 10⁵ Pa·s) detected by rheological characterization (Figure 1c and Supporting Information Figures S78–S89), which was consistent with their macroscopic performances. The zero-shear viscosities of the acid–sugar adhesive materials decreased with the increased temperature, exhibiting the thermosensitive nature of hydrogen-bonding networks and supramolecular polymerization processes. However acid–sugar adhesive materials still had relatively high viscosities at high temperature, which is the basis of their high-temperature adhesion. Temperature-dependent changes of the viscosities were totally reversible. Compared with individual sugars or acids, the newly formed adhesive materials were easier to process. Acid–sugar adhesive materials can be conveniently coated on different surfaces (glass, steel, polymethyl methacrylate [PMMA], and polytetrafluoroethylene [PTFE]) to form uniform adhesion layers with various thicknesses (from tens of microns to several millimeters). Smooth and thin fibers with lengths of several meters were mechanically pulled out from the acid–sugar adhesive materials (Figure 2a), indicating the formation of high-molecular-weight supramolecular polymers.

Adhesion tests were easily carried out because of the good processability of acid–sugar adhesive materials. Using the adhesion on glass as an example, acid–sugar adhesive materials were deposited onto the surface of a glass slice, which was then covered immediately. When weights of up to 70 kg were attached to the glass surface, no separation or displacement of the adhering area (3 × 3 cm²; Figure 2a and Supporting Information Video S3) was observed from shear forces. The adhesion effects of acid–sugar adhesives were not only strong but also long-lasting. Similarly, acid–sugar adhesive materials displayed strong, stable, and long-lasting adhesion effects on other surfaces, from hydrophilic steel to hydrophobic PMMA and PTFE. Recyclable adhesion performances were also realized by acid–sugar adhesive materials.

Quantitative tests were performed to measure the adhesion strengths of acid–sugar adhesive materials on different surfaces and under different conditions (temperature), and to find the relationship between adhesive composition and adhesion effect (Figure 2). The shear strengths on glass surfaces are all higher than 1.10 MPa for all acid–sugar adhesive materials, with malic acid.

### Table 1 | The Components of Supramolecular Adhesive Materials from Natural Acids and Sugars

<table>
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<tr>
<th>Numbers</th>
<th>Acids</th>
<th>Molar Ratios</th>
<th>Sugars</th>
<th>Abbreviations</th>
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<td>D-(-)-fructose (F)</td>
<td>CF</td>
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<td>2</td>
<td></td>
<td>1:1</td>
<td>Sucrose (S)</td>
<td>CS-1</td>
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<td>Sucrose (S)</td>
<td>CS-2</td>
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<td></td>
<td>1:1</td>
<td>D-(-)-glucose (G)</td>
<td>CG</td>
</tr>
<tr>
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<td></td>
<td>1:1</td>
<td>D-(-)-trehalose (T)</td>
<td>CT-1</td>
</tr>
<tr>
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<td></td>
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<td>CT-2</td>
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<tr>
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<td>D-(-)-fructose (F)</td>
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<td>Sucrose (S)</td>
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<td>1:2</td>
<td>D-(-)-trehalose (T)</td>
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Figure 2 | Adhesion strengths of acid-sugar supramolecular adhesive materials. (a) The adhesion process for supramolecular adhesive materials and the macroscopic adhesion behavior. (The adhesion area is 3×3 cm² and the substrate is glass in the right photograph, the weight of the person is 70 kg.) (b–e) Adhesion strengths of acid-sugar supramolecular adhesive materials on iron, glass, PMMA, and PTFE. The dashed lines demonstrate the highest values of adhesion strengths on different surfaces. Error bars show standard deviation of the measured adhesion strengths of acid-sugar supramolecular adhesive materials (n = 4).
fructose (MF) having the highest value at 2.85 MPa. Ultrastrong adhesion effects were obtained between acid–sugar adhesives and steel surfaces. The lowest adhesion strength of acid–sugar adhesive materials on steel was achieved by MF with a value of 3.0 MPa, which is greater than the adhesion strengths of many previously reported supramolecular or polymeric adhesives. Malic acid and glucose (MG) show the strongest adhesion effect on steel, with an adhesion strength at 5.42 MPa. Moreover, acid–sugar adhesive materials exhibited remarkable adhesion capabilities on hydrophobic PMMA. An adhesion strength of up to 1.18 MPa was detected between citric acid and glucose (CG) and PMMA. Though acid–sugar adhesive materials did not show as strong an adhesion capacity on PTFE as that on glass or steel, acid–sugar adhesives still exhibit moderate adhesion strengths on PTFE (from 0.22 to 0.38 MPa; Figure 2e), in comparison with those of commercially available adhesives or previously reported supramolecular adhesives (usually below 0.1 MPa). Acid–sugar adhesive materials are typical supramolecular polymers containing two comonomers (acid and sugar), with hydrogen bonding as the main driving force. Density functional theory (DFT) simulations clearly revealed the three-dimensional networks of hydrogen bonding in acid–sugar complexes (Figure 3a and Supporting Information Figure S91) which drive the supramolecular polymerization between sugars and acids. Owing to the cross-linked polymeric structures and the high density of hydrogen-bonding networks, acid–sugar complexes can strongly bond to hydrophilic surfaces. With the adhesion behavior of MF on glass surface as an example, multiple hydrogen bonds were observed between MF and the glass surface (Figures 3b and 3c). Meanwhile the easy surface spreading and/or gap-filling properties originating from the high-molecular-weight polymeric structures further enhanced the adhesion effects. In addition, abundant carboxylic groups in either malic acid or citric acid were capable of hydrogen bonding with the fluorine groups of PTFE, which leads to effective adhesion behaviors on PTFE.

Though acid–sugar adhesives containing citric acid (citric acid–sugar adhesives) or malic acid (malic acid–sugar adhesives) all exhibited excellent adhesion capacities, the two types of adhesive materials showed several differences in adhesion performance (Figure 2). Citric acid–sugar adhesives had relatively stronger adhesion effects when adhering to hydrophobic surfaces (PMMA and PTFE), compared with malic acid–sugar adhesives. The average adhesion strengths of citric
Figure 4 | Adhesion performances of acid-sugar adhesive materials in organic solvents. (a) Adhesion strengths of CT-2 in different solvents for 24 h. (b) Adhesion strengths of MF in different solvents for 24 h. (c–e) Adhesion strengths of CT-2 in different solvents for 7, 14, and 21 days. (f) Comparison of adhesion strengths of CT-2, MF, and commercially available glues in DCM for 7 days. (g and h) Macroscopic adhesion behavior of CT-2 in DCM. In (h), dye was added to the DCM solution to get a better view. Error bars show standard deviations of the measured adhesion strengths of acid-sugar supramolecular adhesive materials ($n = 4$). Ace, acetone; DCM, dichloromethane; THF, tetrahydrofuran; MeCN, acetonitrile; EA, ethyl acetate.
acid-sugar adhesives on PMMA and PTFE were 1.07 and 0.30 MPa, respectively. These were 34% and 13% higher than that of the corresponding malic acid–sugar adhesives (0.71 and 0.26 MPa). In contrast, malic acid–sugar adhesives were more suitable for adhesion on hydrophilic surfaces, with an average adhesion strength on steel of 4.54 MPa. This average value was higher than the best adhesion value of citric acid–sugar adhesives on steel (CT-2, 4.37 MPa).

When comparing the adhesion effects of all 12 acid–sugar adhesive materials, CT-2, MF, and MG showed relatively stronger adhesion effects than the rest of the adhesive materials. Unfortunately, MG was highly hygroscopic, and the adhesion effect was gradually attenuated. We then focused on CT-2 and MF to further investigate the adhesion capacities of acid–sugar adhesive materials (Figures 2b and 2c). Though both high and low temperatures were responsible for the decay of adhesion strengths of acid–sugar adhesive materials, CT-2 and MF had wide temperature ranges for tough adhesion applications up to 80 °C (Supporting Information Figure S90). When the temperature was kept at 55 °C, the adhesion strength of CT-2 on steel was 4.09 MPa, which is about 93% of that at 25 °C (4.37 MPa). When the temperature was increased to 80 °C, an adhesion strength at 0.43 MPa was still measured, exhibiting the good adhesion capability of CT-2 at high temperature. Similar results were obtained from adhesion tests of CT-2 on other surfaces. MF also has strong adhesion effects at high temperature. In contrast, a total loss of adhesion was observed in our previously reported supramolecular adhesive system driven by hydrogen bonding, when the temperature was increased from 25 to 80 °C.9 These observations demonstrate that the adhesive components were important in the realization of strong adhesion behavior at high temperature.

Tough adhesion at low temperature is an excellent advantage of adhesives for practical applications. CT-2 and MF have strong adhesion abilities at extremely low temperatures, though the low temperature partially weakens the adhesion effects (Supporting Information Figure S90). After storage at −80 °C for 24 h, surfaces were still firmly adhered together by CT-2 or MF. Prolonging the testing time at −80 °C from 24 h to 1 week, no obvious loss of adhesion strengths was observed. For example, CT-2 has an adhesion strength of 4.37 MPa on a steel surface 25 °C, while an adhesion strength of 1.53 MPa was detected by pull-off adhesion tests at −80 °C. More importantly, no decay of adhesion abilities of CT-2 and MF was observed, when the adhesion surface was changed to PTFE (0.22 MPa at 25 °C and 0.25 MPa at −80 °C for CT-2, 0.31 MPa at 25 °C and 0.28 MPa at −80 °C for MF). The adhesion strengths and adhesion effects of CT-2 and MF showed the potential for their application as low-temperature adhesives. The good adhesion capabilities of CT-2 and MF at low temperature can be ascribed to the existence of high-density hydrogen-bonding networks, which makes the adhesives not as fragile as traditional polymeric adhesives at low temperature.54–56

Realizing robust adhesion in organic solvents plays an important role in material science.9,57 Most supramolecular adhesives and polymeric adhesives are either organic solvent-soluble or their adhesion effects are severely attenuated in organic solvents because of swelling.9,56 These drawbacks not only largely restrict the applications of adhesive materials but also greatly hinder the development of material processing. The natural sugars and acids used in this study are insoluble in a variety of common organic solvents, including acetone (Ace), acetonitrile (MeCN), tetrahydrofuran (THF), dichloromethane (DCM), and ethyl acetate (EA). Noncovalently connected acid–sugar adhesive materials have similar solubility behaviors to those of the individual sugars or acids. Solubility tests also confirmed the insoluble nature of the acid–sugar adhesives in various organic solvents. Meanwhile no swelling phenomena were observed when acid–sugar adhesive materials were immersed in different organic solvents.

Based on these observations, it is reasonable to investigate the organic solvent-resistant adhesion behaviors of acid–sugar adhesive materials (Figure 4 and Supporting Information Video S4). Macroscopic long-term adhesion tests demonstrate that after storage in organic solvents (DCM, EA, THF, Ace, and MeCN) for more than 3 months, no separation or displacement was observed when a weight of 2 kg was attached to the adhered glass slices (Figure 4g and Supporting Information Video S5). As shown in Figure 4h, a broken glass tube can be easily repaired by CT-2, which is highly resistant to DCM.9 However, methanol is not suitable for these acid–sugar adhesive materials as it gradually destroys the adhesion effects, which can be ascribed to hydrogen bond formation between methanol and acid–sugar polymeric structures.13,58 Meanwhile, due to the water-soluble properties and hydrogen bond formation of acid–sugar adhesives, adhesion applications under water were not realized. To realize adhesion behavior under water, it is possible to prepare supramolecular adhesives from water-insoluble monomers.

With the adhesion tests in DCM as an example, after storage for 24 h, the adhesion strength of CT-2 on glass is 2.72 MPa (Figure 4a), which is comparable with the DCM-free adhesion values (2.49 MPa). In contrast, commercially available 3M glue and AB glue show negligible adhesion strengths in DCM and other organic solvents (Figure 4f). As shown in Figures 4c–4e, tough adhesion effects are still retained in long-term adhesion tests in organic solvents. After storage in organic solvents for 2 weeks (CT-2 on glass), about 44–60% adhesion strengths were retained, compared with that of solvent-free tests. MF shows even better organic solvent-resistant adhesion capacities. MF on glass and on steel (immersed in organic solvents for
24 h) retains 58–75% and 38–52% adhesion strengths of solvent-free adhesion, respectively (Figure 4b). By comparing with the adhesion strengths obtained in short-term (1 week) and long-term (3 weeks) tests in organic solvents, it is clear that no obvious decay of adhesion strengths took place after long-term exposure to organic solvents. These observations fully demonstrate that acid–sugar adhesive materials are promising as organic solvent-resistant adhesives.

Conclusions

High viscosity is an important issue for DESs, which originates from the three-dimensional hydrogen bond networks and the solvent-free bulk state, while the viscous property and poor fluidity of DESs are considered a serious problem. Therefore, the high viscosity of DESs is always ignored or even avoided. DESs with low viscosity and high fluidity are desirable. In this study, we deliberately used the high viscosity of acid–sugar DESs to realize superior and long-lasting adhesion performances on various surfaces. We reported a family of new adhesive materials consisting of low-molecular-weight natural products. According to the adhesion mechanism and the materials consisting of low-molecular-weight natural sugar adhesive materials, tough and organic solvent-resistant adhesion effects were realized. The hydrogen bond formation between sugars and acids leads to supramolecular polymerization, which triggers the occurrence of strong cohesion effects. A detailed study of organic solvent resistance, polymerization, and supramolecular adhesion of sugar–acid materials was carried out. The formation of cross-linked supramolecular polymeric networks is the basis of the adhesion properties of acid–sugar adhesive materials. Meanwhile, the hydrogen bonding between acid–sugar adhesives and surfaces is the main adhesion interaction. This study dramatically expands the applications of DESs, and sheds light on the development of supramolecular polymeric adhesive materials as promising alternatives to polymeric adhesives.

Supporting Information

Supporting Information is available.

Conflict of Interest

The authors declare no competing financial interest.

Acknowledgments

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