Polyacrylamide-scaffold adhesive bearing multiple benzene rings forming CH/π interactions with polyolefin

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DOI: 10.5185/amlett.2018.2055
www.vbripress.com/aml

Abstract

Adhesion to chemically inert materials (CIM) through non-covalent interactions without surface modifications represents a formidable challenge in adhesion science. We report herein a rigid poly(acrylamide) bearing multiple benzene rings in its side chains that can strongly adhere to the chemically inert surface of the polyolefin without the need for surface modifications. This adhesive is rationally designed based on our previous findings. The adhesion to polyolefin is triggered by the formation of multiple CH/π interactions at the macroscopic interface. The adhesion strength is far greater than that of adhesions using surface modifications or commercially available polyolefin adhesives. In this study, the adhesion mechanism is carefully analyzed by experimental and theoretical studies. We anticipate that this study could address the long-standing issue of achieving strong adhesion to CIMs without requiring surface modifications and pave the way for future research into the development of new adhesives for CIMs. Copyright © 2018 VBRI Press.

Keywords: CH/π interactions, non-covalent interactions, adhesive, adhesion, polyolefin.

Introduction

Polyolefins such as polyethylene (PE) and polypropylene (PP) have been widely used as raw materials in various industrial fields such as packaging materials,(1) optical lenses,(2) lubricants, medical supplies, and automotive components, due to their hypobaricity, low water absorption, low dielectric constant, and high chemical resistance.(3-5) In recent years, polyolefins have received considerable attention as a base film in various cutting-edge composite materials for microfluidic devices,(6) organic field effect transistors,(7) conductive films,(8) biosensors,(9) lithium-ion batteries,(10) solar cells,(11) and others.(12-14) Among various issues in these potential applications, adhesion of the polyolefins is central because poor adhesion causes a dramatic loss of the composite materials' properties. However, adhesion of polyolefins is a formidable challenge because of their chemically inert surface. Efforts to overcome this problem have largely focused on the surface modification of polyolefins.(15-20) Surface modification usually comes at a high cost and entails altering the physical properties and surface configuration of the polyolefin. Therefore, the development of adhesives that do not require surface modification of the polyolefin constitutes a fascinating research area in terms of promoting innovation in materials science and industrial applications.

One promising approach to reach the above objective involves an adhesive based on chemical interactions (AC). To date, several ACs that form non-covalent interactions with polyolefin surfaces have been reported.(12-24) These ACs can strongly adhere to polyolefins without the need for surface modifications. However, most reported examples are limited by the specific structure of the adhesive and its unclear adhesion mechanism. Detailed structural design principles capable of guiding the development of tailored adhesives for target applications have not yet been precisely reported. Therefore, the development of new ACs still depends heavily on serendipitous discovery or random screening; studies based on rationally designed ACs remain extremely rare.

We have recently shown that a rigid polymethacrylate bearing multiple benzene rings in its side chains can adhere to polyolefin through CH/π interactions.(25,26) This hybrid design of multiple benzene rings and a rigid polymer chain plays a crucial role in the adhesion properties. First, the existence of multiple benzene rings confers an advantage in the formation of multiple CH/π interactions. Second, by inhibiting the molecular motion, the rigid polymer chain efficiently promotes the formation of CH/π interactions between the aromatic side chain and the polyolefin, which dissociates the aromatic rings from the polyolefin surface during adhesion. For this reason, poly(tritylmethacrylate) exhibits strong binding to various polyolefins with strengths over 1 MPa without surface modifications. However, the ester bonds of the polymethacrylates are readily cleaved in alcohol, particularly under acidic conditions, which makes it difficult to study and stably use the polymers for extended periods of time. This essential problem may hamper practical applications of our ACs. Amide bonds are usually stronger than the corresponding ester bonds against hydrolysis.

Herein, we developed a novel polyacrylamide-type adhesive that can strongly adhere to polyolefins through CH/π interactions without the need for surface modifications (**Fig. 1**). This adhesive was rationally designed based on our previous findings. The adhesion of polyacrylamide-type adhesives to polyolefins is far stronger than the approaches using surface modification and commercially available polyolefin adhesives, creating a more effective approach for the adhesion of polyolefins. The macroscopic interface between our adhesive and polyolefin was carefully analyzed based on experimental and theoretical studies. We expect our study to aid in the further development of new adhesives for polyolefins.

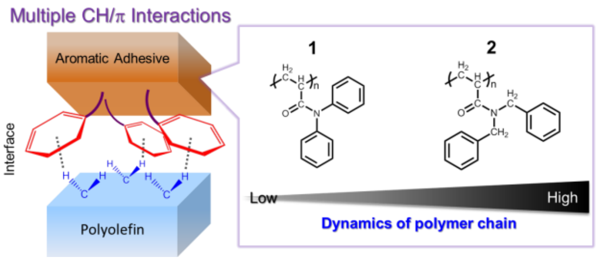

Fig. 1. Schematic illustration of adhesion based on CH/π interactions and molecular structures of adhesives **1**–**2**.

Experimental

All experimental procedures are reported in the Supporting Information.

Results and discussion

Adhesives 1-2

We have recently shown that the hybrid design of multiple benzene rings in side chains and the rigid polymer chains of polymethacrylate are important for the structural design of superior adhesives in our system.(25,26) Based on these previous findings, we designed poly(*N*, *N*-diphenyl acrylamide) (**1**) as an amide-type adhesive. First, **1** has multiple benzene rings in its side chains. Second, the close proximity of bulky di-phenyl groups to the polyacrylamide main chains inhibits flexibility and induces a rigid structure. For comparison, poly(*N*,*N*-dibenzyl acrylamide) (**2**) was also selected as a flexible polymer. Each monomer of adhesives **1** and **2** was prepared via a one-step reaction between the corresponding diaryl amine and acryloyl chloride in good yield. Polymeric adhesives **1** and **2** were synthesized by the thermal radical polymerization of each monomer. The number-averaged molecular weights (M_n) and polydispersity indices (PDI) are 24.4 kDa and 1.68 for **1** and 24.7 kDa and 1.59 for **2,** respectively (**Table 1**).

Table 1. M_n, PDI, T_g, and T_1 values for the methine groups of adhesives **1** and **2.**

Adhesive	M_n(kDa)	PDI	T_g (°C)	T_1(sec)
1	24.4	1.68	222	0.89
2	24.7	1.59	91	2.23

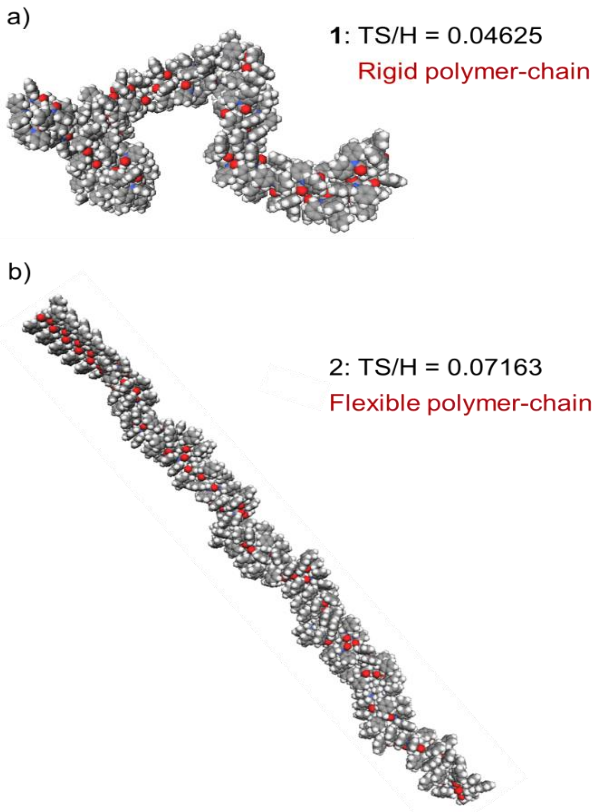

Fig. 2. Stable structures of **1** (a) and **2** (b) obtained by the MM method.

Differential scanning calorimetry (DSC) measurements, nuclear magnetic resonance (NMR) spectroscopy, and a molecular modelling study confirmed that **1** is a rigid polymer and **2** is a flexible polymer. In the DSC measurements shown in **Table 1**, the glass-transition temperature (T_g) of **1** (222 °C) is much higher than that of **2** (91 °C). Moreover, in the ^{1}H NMR spectrum, the spin-lattice (T_1) relaxation time (0.89 s) of the main-chain methine peaks (2.62 ppm) of **1** is lower than that of **2** (2.90 ppm, 2.23 s). These results show that the polymer-chain mobility of **1** is lower than that of **2**. A molecular modelling study strongly supports these experimental results. The stable structures with 100 repeating units of adhesives **1** and **2** were calculated by the molecular mechanics (MM) method at the universal force field (UFF) level of theory (**Fig. 2**). We then carried out a thermal vibrational calculation using the stable structures of **1** and **2**. Previously, we investigated the dynamics of polymer chains through the ratio of entropy to enthalpy (TS/H) obtained from thermal vibrational calculations.(26) Using this approach, the calculated TS/H value is 0.04625 for **1** and 0.07163 for **2**. This result indicates that the polymer-chain dynamics of **1** are lower than that of **2**. The correlation between the type of polymer and adhesives **1** and **2** is summarized in **Fig. 1**.

Adhesion of adhesives to PE

Among various polyolefin resins, we selected polyethylene (PE) because it is the most common mass-produced plastic. Adhesion interfaces between the PE substrate and adhesives **1** and **2** were fabricated using the bar-coating method. The adhesive layers on each PE sample were characterized by attenuated total reflection (ATR)-Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements. The IR spectra showed characteristic peaks at around 1665 cm^{-1} ($\nu_{C=O}$) and 3000–3100 cm^{-1} (ν_{CH}; aromatic ring), which were assigned to the carbonyl groups of the amide and aromatic rings, respectively. In the XPS spectra, two characteristic C 1s peaks at 287 eV (N-C=O) and 288–292 eV (π–π*) were observed, corresponding to the carbonyl of the amide and aromatic groups, respectively. In addition, one characteristic N 1s peak at 400 eV was observed, corresponding to the amide. The thicknesses of the adhesive layers were in the range of 352–390 nm, as determined by field emission scanning electron microscopy (FE-SEM).

Next, we investigated the polymer-chain structure of the adhesives on the PE surface by ATR-FTIR. **Fig. 3a** depicts the different absorption spectra obtained when the spectrum of PE was subtracted from that of the prepared samples. The investigation was completed based on the results of density functional theory (DFT) calculations. The *trans* and *cis* conformations of the main chain were assigned based on the absorption bands at 1075 cm^{-1} and 1100 cm^{-1}, respectively. Rigid polymer **1** shows a strong absorption peak at 1075 cm^{-1} and a smaller peak at 1100 cm^{-1}. Thus, we concluded that **1** forms extended polymer chain structures on the PE surface. In contrast, flexible polymer **2** was observed to have an absorption peak at 1100 cm^{-1} in addition to the absorption at 1075 cm^{-1}. Thus, we concluded that polymer **2** has a random coil structure on the PE surface. Previously, we demonstrated that the extended polymer chain structure of the adhesive is advantageous to the formation of multiple CH/π interactions with the PE surface.(26) Therefore, we speculate that **1** can effectively engage in multiple CH/π interactions with the PE surface and exhibits stronger adhesion to PE than **2**.

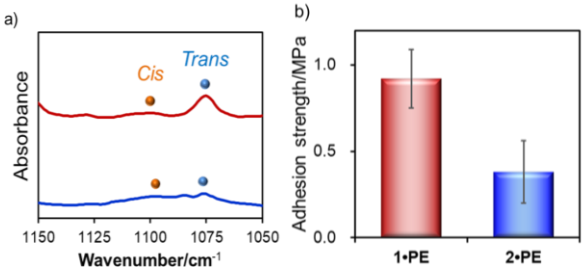

Fig. 3. (a) FT-IR absorption spectra associated with the *cis* and *trans* backbone conformations of polymers **1** and **2** on PE. (b) Adhesion strength (MPa) of **1** and **2** to PE determined via lap-shear measurement. Error bars represent one standard deviation for n = 5.

The interfacial adhesion between the PE substrate and the adhesives was investigated by lap-shear testing, with the adhesion failure point confirmed by ATR-FTIR and XPS measurements. After adhesion testing, no amide groups or aromatic groups were detected at the PE surface for all samples, implying that adhesion failure occurred at the PE–adhesive interface since no internal breakages were observed. The interfacial adhesion strengths (MPa), which are the averages of 5 replicate tests, are shown in **Fig. 3b**. Rigid polymer **1** exhibited stronger adhesion to PE (0.92 MPa) than flexible polymer **2** (0.38 MPa). The adhesion strength of **1** to PE is comparable to that of our previously reported poly(methacrylate)-type adhesive (1.11 MPa).(26) Compared with approaches that use commercially available adhesives and surface modifications, we found that **1** held a significant advantage. We recently showed that commercially available adhesives (urethane and silicone types) for polyolefin adhere to PE with a strength of 0.61 MPa and 0.55 MPa, respectively.(26) Cho et al. reported that the adhesion of polysiloxane to surface-activated polyolefin via oxygen plasma treatment has a strength of 0.43 MPa.(27) The adhesion strength of adhesive **1** to polyolefin is far greater than adhesions using surface modifications and commercially available polyolefin adhesives.

Adhesion mechanism

We performed modelling studies based on molecular dynamics (MD) simulations to investigate the adhesion behavior of adhesives **1** and **2** to PE. The simulation was performed using a model system composed of a single-phase PE sheet constructed based on X-ray diffraction (XRD) data and the stable adhesive structures obtained via MM calculations. **Movies S1** and **S2** show the results of the MD simulations for polymers **1** and **2**, respectively. **Fig. 4a** and **Fig. 4b** show the typical structures of **1** and **2** obtained after a 150-ps simulation at 298 K and 1 atm. We estimated the statistical averages of the interfacial interaction energies (ΔG) between the adhesives and the PE surface in the MD simulations, which equal −48.3 and −38.5 kcal mol^{-1} for polymers **1** and **2**, respectively (**Fig. 4c**). These results indicate that **1** clearly forms a more stable adsorbed state than **2**. The interfacial interaction energies (ΔG) are related to the overall polymer adhesion strengths.

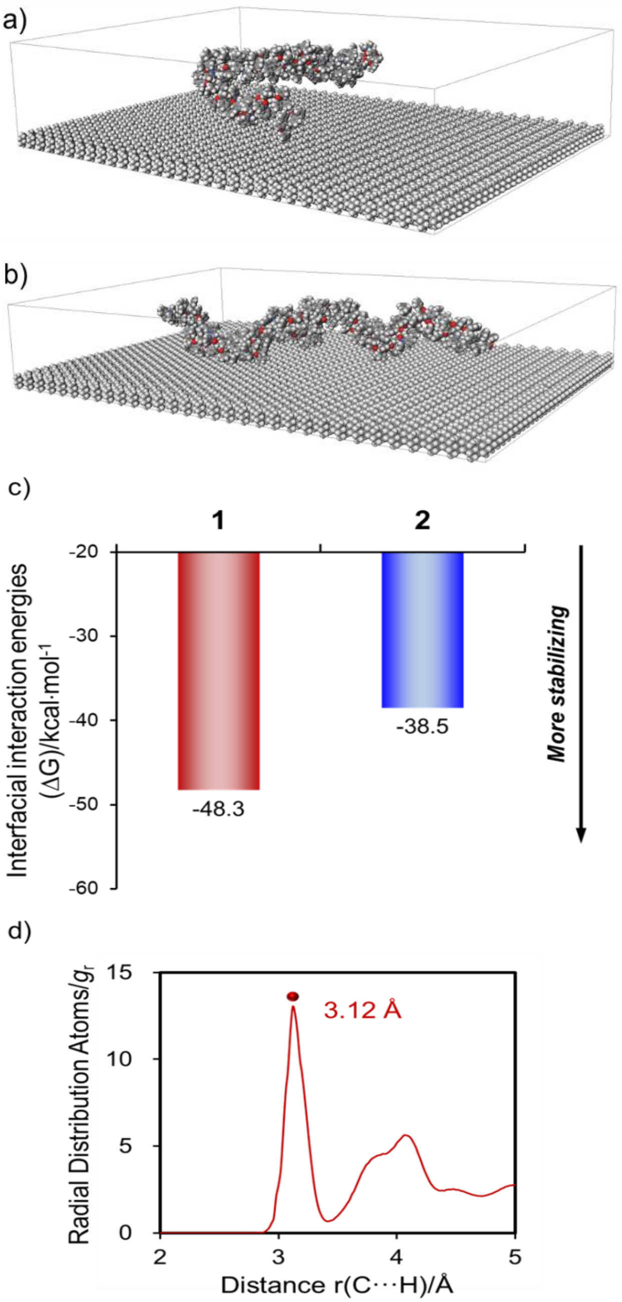

Fig. 4. Typical structure of (a) **1** and (b) **2** on PE after 150-ps MD simulations. (c) Average interfacial interaction energies (ΔG) between the adhesives and the PE surface in the MD simulations. (d) Statistical average of RDFs (g_r) as a function of the distance (r) between the C atoms of the benzene rings of **1** and the H atoms of the PE surface in the MD simulations.

To investigate the formation of the CH/π interactions between adhesive **1** and PE, we determined the relationship between the statistical average of the radial distribution function (RDF (g_r)), and the distance ($r_{C\cdots H}$) between the C atoms of the benzene rings of adhesive **1** and the H atoms on the PE surface in the MD simulations (**Fig. 4d**). Major peaks for **1** were observed at 3.12 Å. A previous study on CH/π interactions established that the optimal C$\cdots$H distance is around 3.0 Å.(28) Therefore, we assigned the first peak in **1** to the average distance between the C atoms of the naphthalene rings and the H atoms of PE that are restrained by CH/π interactions. Based on the results obtained from these theoretical studies, we concluded that the adhesion of polymer **1** and PE is triggered by CH/π interactions between the benzene rings and alkyl groups.

Conclusion

In summary, we have developed a poly(acrylamide)-type adhesive (**1**) that adheres to the chemically inert surface of polyolefin without the need for surface modifications. The adhesive was rationally designed based on our previous findings. Interfacial analysis indicated that the adhesion of polymer **1** to polyolefin is triggered by CH/π interactions. The rigid polymer structure and multiple benzene rings of polymer **1** enhance the formation of multiple CH/π interactions with the polyolefin. Further enhancements of the adhesive properties of this polymeric adhesive as well as possible practical applications are now being investigated.

Acknowledgements

This work was supported by Nisso Chemical Analysis Service Co., Ltd. We would like to thank Editage (www.editage.jp) for English language editing.

Author's contributions

Conceived the plan: TY, HS, MA; Performed the experiments: TY, TF, TY; Data analysis: TY, TF, TY, MA; Wrote the paper: TY (TY, HS, TF, TY, MA are the initials of authors). Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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