

Strong, Removable, and Photoluminescent Hyperbranched Polyamide-amine Hot Melt Adhesive

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Electronic Supplementary Information

Abstract The development of adhesive technology is gaining increasing attention in machinery, electronics, aviation, and other fields. However, traditional adhesives are difficult to be peeled and removed after cross-linking and curing due to the limited solubility in common solvents, which causes pollution and damage to the surface of the adherend. In this work, we synthesized random hyperbranched polyamide-amine hot melt adhesives through Michael addition of 1,8-octanediamine and *N,N'*-methylene diacrylamide (ODA-RHP HMA). Owing to the presence of various polar groups, ODA-RHP HMA exhibited robust lap shear strength to different substrates, including glass (6.6 MPa), ceramics (10.3 MPa), steel (11.5 MPa), and aluminum (11.8 MPa). Due to the hydrogen bonds in ODA-RHP, the HMA demonstrated intrinsic self-healing ability, which can be used repeatedly when being subjected to cyclic heating and cooling. Since ODA-RHP HMA can be swollen or dissolved in ethanol, the adhesives can be easily removed through erasing. In addition, ODA-RHP exhibited aggregation-induced luminescence due to the tertiary amine structure in the molecular structure of ODA-RHP, which can be used in the field of cultural relics restoration.

Keywords Hot melt adhesive; Polyamide-amine; Reusability; Cultural relics restoration

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INTRODUCTION

With the development of adhesive technology, the demand and consumption of adhesives are gradually increasing. Adhesives with high transparency, excellent mechanical properties, and reworkability are highly desirable for bonding metal, wood, and engineering plastics.^[1] Traditional adhesives, including epoxy resins, organosilicons, phenol-formaldehyde resins, and urea-formaldehyde resins, are widely used in machinery, electronics, aviation, and other fields.^[2] However, these adhesives are poorly soluble in common solvents due to their cross-linked structure,^[3–5] and thus they are difficult to recycle and remove. Simultaneously, due to the extensive use of adhesives, it has caused great pollution to the environment.^[6] Therefore, there is an urgent need to develop a removable and pollution-free adhesive.

In recent years, hot melt adhesives (HMA) have been widely used in daily life and industries.^[7] Compared with other adhesives, they are easy to transport and store, and do not con-

tain organic solvents to avoid the emission of volatile organic compounds.^[8,9] Therefore, they are more environmentally friendly than traditional adhesives. Polyurethane HMA is commonly used which can exhibit the adhesive ability to a variety of materials. Polyurethane HMA is divided into thermoplastic polyurethane (TPU-HMA) and reactive polyurethane (PUR-HMA).^[10] TPU-HMA flows when heated and can be fixed upon cooling, which is capable of reversible adhesion. However, its heat and chemical resistance, as well as bonding properties are poor due to the linear structure. PUR-HMA refers to linear polyurethane with low molecular weight and isocyanate-terminated groups, by which the isocyanate group can react with many functional groups for interface chemical bonds. Compared with TPU-HMA, PUR-HMA usually shows higher adhesive strength and better heat and chemical resistance. However, its curing speed is so slow that it requires a few days to form stable adhesion to different substrates. Furthermore, due to the reactive isocyanate groups, the storage and transport of PUR-HMA face various challenges.^[11] The introduction of dynamic covalent bonds into the polyurethane system might produce adhesives with the combined advantages of TPU-HMA and PUR-HMA.^[12] You's group used reversible oxime-carbamate bonds to build a dynamically crosslinked polyurethane HMA.^[13] It featured chemical resistance and

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possessed the ability to bond and debond on demand. However, due to its solvent resistance, the remaining HMA was poorly soluble in the solvent, which made it difficult to clean up for the recycle of the substrates. Therefore, the development of HMAs with adequate adhesive strength, facile recycle and cleaning process is on-demand.

Linear polyamide has the characteristics of regular structure, symmetry, and low steric hindrance.^[14] However, due to the high polarity of the amide group, linear polyamide is easy to crystallize with high melting point and poor solubility, which limits their applications as HMA.^[15] Wu's group synthesized a random hyperbranched polyamide-amine by the Michael addition reaction of 1,4-butanediamine and *N,N*-methylene diacrylamide (MBA).^[16] Owing to the high-density multiple hydrogen bonds, random hyperbranched polyamide-amine showed excellent characteristics of self-healing at room temperature. This work inspired us to apply the random hyperbranched polyamide-amine to the field of HMA. The hyperbranched structure may endow it with better solubility due to its numerous terminal amino groups.^[17–23] Moreover, the abundant polar terminal groups in the hyperbranched polyamide-amine may show good bonding properties to the surface of many polar materials,^[24–26] among which high-density multiple hydrogen bonds are beneficial to provide greater adhesive strength.

In this work, hyperbranched polyamide-amine HMA with outstanding bonding properties was prepared through Michael addition reaction of MBA and amines. We used 1,8-octanediamine and MBA to synthesize a random hyperbranched polyamide-amine (ODA-RHP). Due to its unique random hyperbranched structure, it is easily soluble in the green solvent, and the residual HMA on the substrates could be wiped and removed efficiently without any damage to the surface of the materials. In addition, the synthesized ODA-RHP features aggregation-induced luminescence, which can be used for accurate fluorescent tracking of bonding positions in cultural relics restoration.^[27–30]

EXPERIMENTAL

General Considerations

N,N-methylene diacrylamide (MBA, 99%), 1,8-octanediamine (ODA, 98%), ethylenediamine (EDA, 99%) and 1,4-butanediamine (BDA, 98%) were purchased from Aladdin. Methanol was purchased from Guanghai Technology Corporation. Acetone was purchased from Sinopharm Chemical Reagent. All the chemicals were used as received without further purification. 3MPU-2665 and 3MPA-3779 were purchased from 3M Corporation. LoctitePA-6239 was purchased from Henkel Corporation.

Synthesis of Regular Hyperbranched Polymers and Film Preparation

The randomly hyperbranched polymers (RHP) were synthesized by one-pot method through Michael addition reaction between MBA and ODA. The molar ratio of MBA:ODA in the reaction is 1:1.125. In a typical procedure, the synthesis of RHP was described as follows: MBA (12.332 g, 1 equiv.) was added into a round bottom flask containing mixed solvent of 60 mL of methanol and 30 mL of deionized water at 30 °C and stirred until it was dissolved totally. Then, ODA (12.98 g, 1 equiv.) was

fed into the flask directly. The mixture was stirred at 30 °C for 24 h. After that, the solution was poured into a beaker containing 1000 mL of acetone for precipitation. The crude product was washed for 3 times with acetone and then dried in a vacuum oven at 30 °C for 48 h. The comparison samples were synthesized using the same procedure with EDA or BDA replacing ODA. In a typical process, 1.4 g of ODA-RHP was dissolved totally in 10 mL of methanol. The solution was poured on a PET plate. The transparent film of ODA-RHP obtained by methanol was completely volatilized at room temperature.

General Characterizations

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (Advance III) 400 MHz in deuterated methanol solution. The melting point temperature (T_m) was tested by differential scanning calorimetry (DSC) which was performed on NETZSCH DSC 200PC instrument. All of the samples were first heated from 30 °C to 120 °C at 10 °C·min⁻¹ and then rapidly cooled to -110 °C with an empty aluminum pan as the reference. Then, all data were collected during a second heating run at a scanning rate of 10 °C·min⁻¹ from -110 °C to 200 °C under a dry nitrogen atmosphere. The SAXS measurement was performed on a SAXS instrument (Anton Paar SAXS point 2.0) equipped with a Cu/Mo dual micro focal X-ray source and a 2D hybrid photon counting detector (EIGER R 1M). The long period (L) was obtained by Bragg's law: $L = 2\pi/q$, where q is the value of the peak in the intensity curves ($I(q)-q$). X-ray diffraction (XRD) characterization was performed using XRD-6100 (Shimadzu XRD-6100, Japan) with Cu K α radiation. The data were collected between 10° and 60° with a scanning speed of 10 (°)·min⁻¹. The temperature sweep experiment was performed on a rheometer (MCR302; Anton Paar, Graz, Austria) between 80 and 180 °C to measure the storage modulus and the loss modulus. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer 100 serial FTIR spectrophotometer equipped with universal attenuated total reflectance (ATR). The sample powder was placed in the sample cell and measured directly. The data scan range is 400–4000 cm⁻¹, sampling 32 times, and the test resolution is 4 cm⁻¹. TGA measurements were performed in the NETZSCH TG209C (NETZSCH Corporation, Germany) via scanning a temperature range from 35 °C to 600 °C (10 °C·min⁻¹) under flowing nitrogen gas and air using an alumina crucible. PL emission spectra was recorded on a fluorometer (Edinburgh FLS 980) at an excitation wavelength of 360 nm. Lifetimes (τ) were acquired with the QM/TM/IM steady-state & time-resolved fluorometer. The UV absorption spectra were performed on an UV-Vis spectrophotometer (PE Lambda950, Instrument Analysis Center of Xi'an Jiaotong University).

Lap Shear Tests

ODA-RHP HMA was placed between two identical substrates and the overlapping area was measured. The two substrates were pressed gently and held by two binder clips and cured in an oven at 160 °C for 45 min and then cooled down to room temperature. Lap shear testing was used to evaluate the adhesion properties, which was performed on a universal testing machine (CMT 5305). Umbonded specimens were extended at a speed of 10 mm·min⁻¹ at 25 °C. The force was measured via a 5000 N capacity load cell. The displacement was measured by displacement sensor in the universal testing machine. The repeated adhesive testing of ODA-RHP HMA was

tested by gluing aluminum plates. The ODA-RHP HMA bonded aluminum plates were subjected to a lap-shear test until failure; the two separated sheets were reassembled and heated in an oven at 160 °C for 45 min to form the new connection. Then the bonded aluminum plates were subjected to the lap-shear test again.

RESULTS AND DISCUSSION

Synthesis and Characterization of ODA-RHP

ODA-RHP was synthesized by one-pot Michael addition between 1,8-octanediamine (ODA) and *N,N'*-methylene

diacrylamide (MBA) (Fig. 1a). The molecular structure of ODA-RHP was verified by $^1\text{H-NMR}$ spectra (Fig. S1 in the electronic supplementary information, ESI). The typical proton signals at 6.0 and 5.6 ppm corresponding to vinyl groups disappeared after reaction, while new signals appeared at 2–3 ppm belonging to the methylene of $-\text{CH}_2-\text{CH}_2-\text{CONH}-$ in ODA-RHP, which indicated that all the vinyl groups were completely consumed. The proposed hydrogen bond interactions of the ODA-RHP were shown in Fig. 1(b), and the multiple hydrogen bonding of ODA-RHP contributed to its adhesive properties to different substrates. The $\text{N}-\text{H}$, $-\text{NH}_2$ and $\text{C}=\text{O}$ groups can form hydrogen bonds with solid materials to improve the

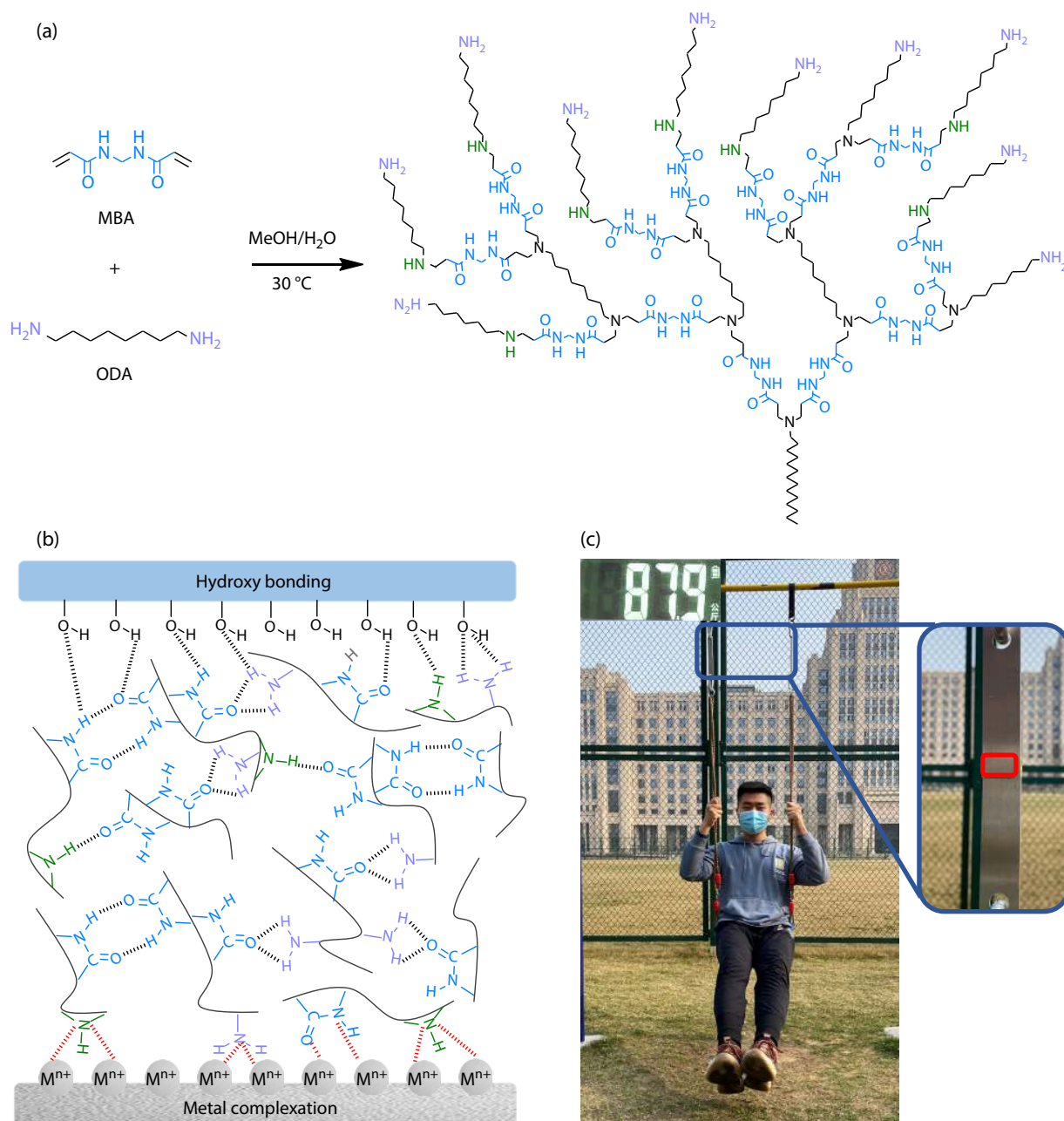


Fig. 1 (a) Synthesis of ODA-RHP through Michael addition between ODA and MBA. (b) Schematic diagram of the adhesive mechanism of the ODA-RHP. (c) Photograph of two pairs of bonded aluminum substrates with ODA-RHP to withstand an adult (approximately 88 kg, the bond area was 2.5 cm²).

adhesion,^[31,32] and the N—H, —NH₂ and C=O groups of ODA-RHP can generate metal complexation with the metal ions on the solid surface for adhesion.^[33] As depicted in Fig. 1(c), two pairs of bonded aluminum substrates by ODA-RHP could withstand an adult human with the weight of approximately 88 kg, demonstrating the outstanding adhesiveness of ODA-RHP.

For comparison, other RHPs were synthesized using different diamines and MBA. Ethylenediamine (EDA) and 1,4-butanedi-amine (BDA) reacted with MBA to synthesize RHPs, respectively. The thermodynamic properties of the RHP materials were carried out by DSC measurements (Fig. S2 in ESI). It is revealed that the melting temperatures (T_m) of ODA-RHP (150 °C) was higher than those of EDA-RHA (90 °C) and BDA-RHP (120 °C), which may be due to the higher crystallinity of ODA-RHP. As demonstrated in Fig. 2(a), the small-angle SAXS tests of the film samples showed that there were microphase separations in the ODA-RHP (in the order of 4.2–20.9 nm). However, this phenomenon was not obvious in EDA-RHP and BDA-RHP samples. XRD measurement also verified the sharp crystallization capability of ODA-RHP (Fig. S3 in ESI). The crystalline micro-domains can improve the mechanical strength of the material, which may be beneficial to the adhesive strength.^[14] Then the adhesive properties of the RHP HMAs were evaluated by the lap shear test. A typical adhesion sub-

strate of aluminum sheet was used, and the substrates and RHP HMA were held together by binder clips, which were placed in the ovens at 100, 130, 160 °C for EDA-RHP, BDA-RHP, and ODA-RHP HMA, respectively. The curing temperature was slightly higher than the melting point temperature of RHPs, at which the HMAs can be completely melted. The bonding area was 2.5 cm × 1.0 cm, and the thickness of the RHP HMA films was 0.1 mm. After 45 min, they were taken out and cooled to room temperature. The test results of the shear bond strength of these materials were shown in Fig. 2(b). We found that ODA-RHP HMA showed better adhesive strength (11.36 ± 0.3 MPa) than those by BDA-RHP HMA (8.71 ± 0.6 MPa) and EDA-RHP (7.11 ± 0.5 MPa). The polar groups in RHP HMAs could lead to the formation of various non-covalent interactions with substrates, and the enhanced crystallization capability of ODA-RHP with predictably high mechanical property may be beneficial to the improved adhesive strength.

A temperature sweep experiment was conducted by rheometer to evaluate the change of moduli of ODA-RHP (Fig. 2c). When the temperature was higher than 90 °C, the modulus of ODA-RHP significantly dropped, implying that the H-bonds in ODA-RHP dissociated and the crosslinked network was partially destroyed. The intersection of the storage modulus (G') and the loss modulus (G'') at 150 °C indicated that ODA-RHP

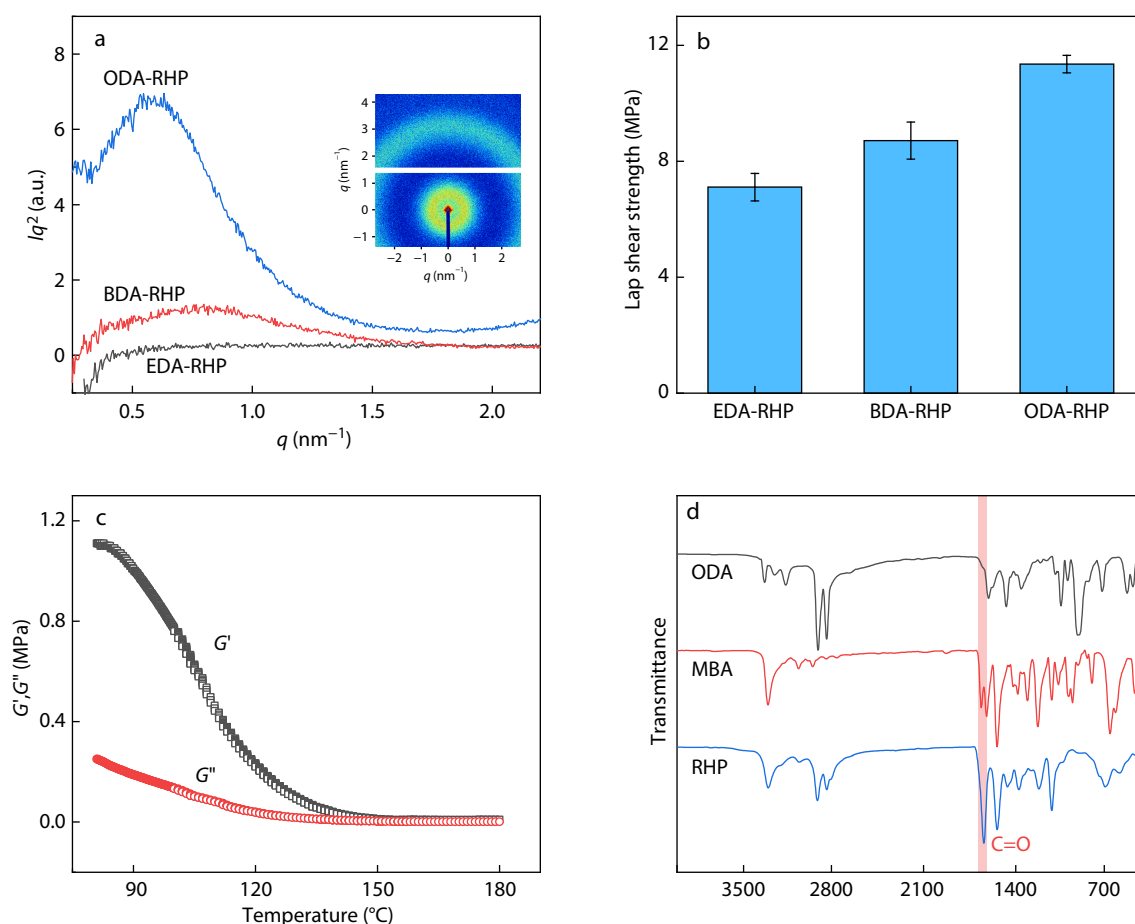


Fig. 2 (a) Small-angle X-ray scattering (SAXS) profile of a series of RHP. The inset shows the two-dimensional (2D) SAXS image of ODA-RHP. (b) Comparison of adhesive properties of RHPs. (c) Storage modulus (G') and loss modulus (G'') of ODA-RHP versus temperature. (d) FTIR spectra of ODA, MBA and ODA-RHP.

transformed from elastic-like behavior to liquid-like behavior. The adhesive strength of the material is determined by its mechanical performance and the interface effect with the bonded substrates.^[34] After subjecting to a lap-shear test, the remaining ODA-RHP HMA on the glass substrates were shown in Fig. S4 (in ESI). The ODA-RHP material was destroyed, which proved that the influence of mechanical performance was more critical than the interface effect. For comparison, EDA-RHP and BDA-RHP were also tested by temperature scanning rheometer. As shown in Fig. S5 (in ESI), the storage moduli of EDA-RHP and BDA-RHP were significantly lower than that of ODA-RHP. ODA-RHP with high storage moduli is beneficial to the improved adhesive strength. We then employed FTIR spectra to investigate the hydrogen bond formation in ODA-RHP. As shown in Fig. 2(d), the characteristic bands at 3309, 1664, and 1535 cm^{-1} belong to the strong stretching vibration of N—H group, C=O stretching vibration band and N—H bending vibration band in MBA, respectively. However, in the FTIR spectrum of ODA-RHP, the characteristic amide I and amide II bands shifted to 1641 and 1531 cm^{-1} , respectively, which were attributed to the formation of the hydrogen bonds.^[35] Thermogravimetric analysis (TGA) was used to test the thermostability of ODA-RHP. The result in Fig. S6 (in ESI) shows that the $T_{5\%}$ (the 5% weight loss temperature) of ODA-RHP is as high as 253 $^{\circ}\text{C}$, suggesting the vast poten-

tial as adhesive agents in normal working conditions.

Adhesive Properties of ODA-RHP HMA

In order to reduce the oxidation of amine groups at high temperature, we prepared the film at room temperature. The ODA-RHP powders were dissolved in methanol and then the solution was added dropwise onto the polyethylene glycol terephthalate (PET) plate. After the methanol was completely volatilized, a colorless and transparent film was obtained. Then, the adhesion properties of the ODA-RHP HMA were tested by the lap shear test. The bonding area was 2.5 $\text{cm} \times 1.0 \text{ cm}$ and the thickness of the RHP HMA films was 0.1 mm. The schematic diagram of the bonding process is shown in Fig. 3(a). The effect of curing time and curing temperature on the bonding strength of lap joints was analyzed, and the optimal bonding conditions were established. As shown in Fig. S7 (in ESI), we found that the bond strength increased with the curing time, and the maximum bond strength was $11.4 \pm 0.4 \text{ MPa}$ when the curing time was 45 min. However, when the curing time was longer than 45 min, the bonding strength decreased, and the bonding strength was $8.55 \pm 0.7 \text{ MPa}$ when the curing time was 120 min. This may be caused by the oxidation of the amine groups when ODA-RHP was incubated at high temperature for a long time. Moreover, when the curing time was 15 min, the bonding strength of ODA-RHP HMA reached 10 MPa, which indicated that the shorter curing time was efficient for the adhesive

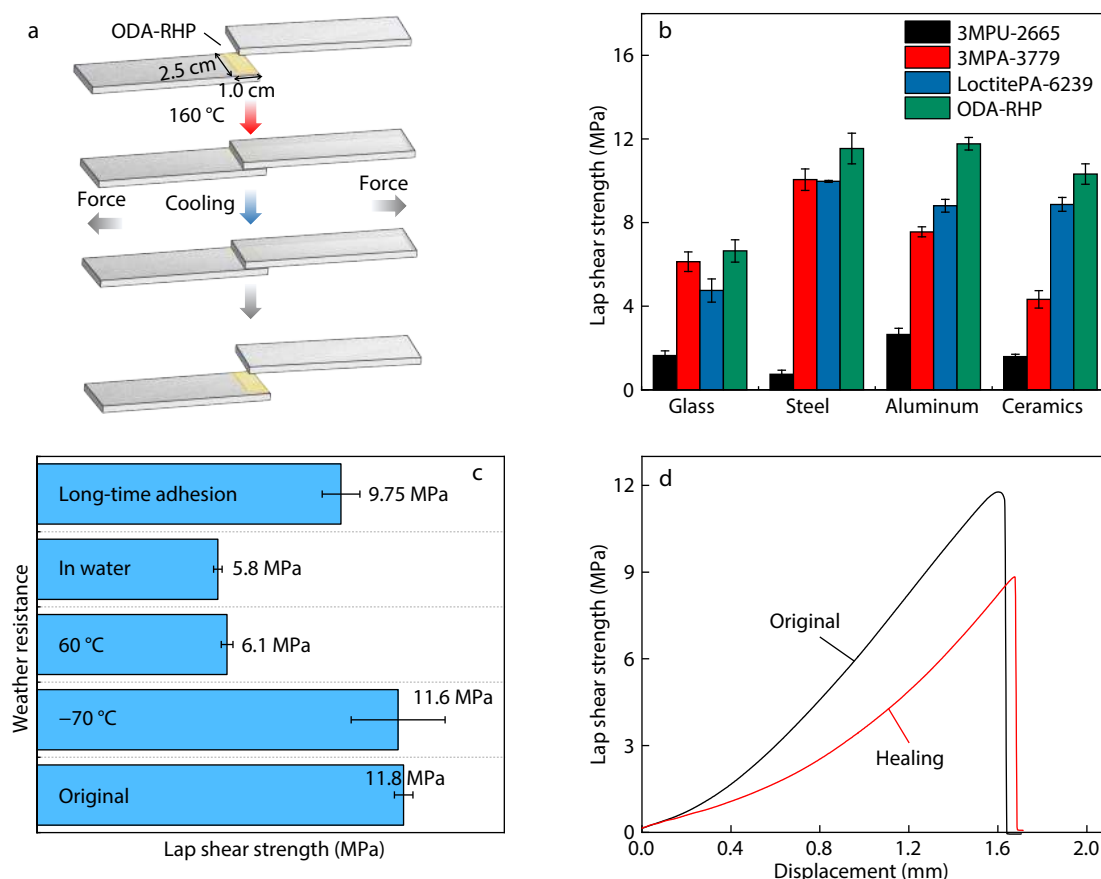


Fig. 3 Adhesive properties of ODA-RHP HMA. (a) Schematic diagram of the adhesive procedure; (b) Comparison of lap shear strength of ODA-RHP and commercial HMA with different substrates; (c) Weather resistance of ODA-RHP HMA; (d) Lap shear strength of the original and healing samples.

behavior. Furthermore, we investigated the adhesive strength of ODA-RHP at different temperatures. It was found that the bonding strength of ODA-RHP became stronger with the increase of temperature (Fig. S8 in ESI). When the curing temperature was 160 °C, the bonding strength was as high as 11.4 MPa. Therefore, we selected the curing time of 45 min and the curing temperature of 160 °C for the adhesive study. In order to demonstrate the superior bonding properties of ODA-RHP HMA, it was compared with different kinds of commercial polyurethane (PU) and polyamide (PA) HMA, including 3MPU-2665, 3MPA-3779 and LoctitePA-6239. The results of the lap shear test are shown in Fig. 3(b). Clearly, ODA-RHP demonstrated a higher adhesive strength than other commercial HMAs with different substrates, including aluminum plates, steel plates, glass plates and ceramic materials, of which the adhesive strength can achieve 11.6, 11.54, 6.64 and 10.32 MPa, respectively. The bonded aluminum, steel, and ceramics samples exhibited higher lap shear strength, possibly owing to their rough surfaces. Especially for metals substrates, the N—H, —NH₂ and C=O groups of ODA-RHP can generate metal complexation with the metal ions on the aluminum and steel surface in addition to hydrogen bonding.^[33]

The weather resistance of adhesive agents is of importance for practical applications. The bonded aluminum plates were placed at room temperature for 14 days, followed by lap shear testing to investigate the long-term stability of ODA-RHP HMA. It was found that the lap shear strength could still maintain as high as 9.75±0.61 MPa (Fig. 3c). We then evaluated the water-resistance of ODA-RHP HMA. The result showed that the lap shear strength of the bonded aluminum plates was 5.8±0.13 MPa after immersing in water for 10 h, which may be due to the swelling of ODA-RHP. However, it was still higher than the bonding strength of many HMAs, such as 3MPU-2665 (2.7±0.29 MPa). Moreover, even after being placed at 60 °C for 10 h, the lap shear strength can still reach 6.1 MPa. Liu *et al.* reported a self-healing supramolecular polyurethane (PU) as HMA to glue diverse materials with high adhesive strength.^[36] However, the adhesive strength of the PU HMA was 3.1 MPa at low-temperature compared to the original adhesion strength of 7.24 MPa. In our work, the bonded aluminum plates were placed in different environments to test their weather resistance. The results showed that ODA-RHP HMA featured excellent low temperature resistance, and the lap shear strength was 11.6±1.50 MPa after being placed at −70 °C for 10 h. Furthermore, due to the rapid reconstruction of hydrogen bonds, we also performed the repeated adhesive testing to demonstrate the reusability of ODA-RHP HMA. The ODA-RHP HMA bonded aluminum plates were subjected to a lap-shear test until failure; the two separated sheets were reassembled and heated in an oven at 160 °C for 45 min to form the new connection. As shown in Fig. 3(d), the adhesive strength can still reach 8.82 MPa, which is comparable to that of the original adhesion strength (11.6 MPa), and the self-healing efficiency is 76%. Overall, it can be found that the adhesive properties of ODA-RHP HMA were stronger than those of general commercial adhesives, and it exhibited weather resistance under different conditions. Such notable properties make it promising adhesives in the fields of machinery, automotive, and electronics.

Applications of ODA-RHP HMA

It was found that the ODA-RHP films exhibited blue luminescence under irradiation with a wavelength of 365 nm (Fig. S9 in ESI), which could be explained by aggregation-induced emission (AIE).^[37–40] The small molecules and polymers, such as poly(amidoamine) dendrimer and poly(ethyleneimine) with tertiary amine structures, can emit strong blue fluorescence, which is non-traditional emission and closely related to $n-\pi^*$ interactions among the electron-rich groups.^[40–42] The key reason for the strong blue luminescence may be due to the tertiary amine structure in the molecular structure of ODA-RHP. The ODA-RHP powders were dissolved in methanol to obtain ODA-RHP solutions with different concentrations to test their fluorescence properties. It was found that the diluted ODA-RHP solutions (less than 1 wt%) presented almost no absorption, while the concentrated solutions showed remarkably enhanced absorption with a new peak appearing at 280 nm (Fig. S10 in ESI), which could be considered as the formation of aggregates. It was also verified by the fluorescence enhancement of ODA-RHP in mixed solvents (good solvent is ethanol and poor solvent is acetone; Fig. S11 in ESI). As shown in Fig. 4(a), the gradual increase in fluorescence intensity also proved the AIE of ODA-RHP, and the inset was a photograph of the fluorescence intensity of ODA-RHP solution with different concentrations (10^{−5}%, 0.1%, 1%, 5%, 10%, and 15%, from left to right). As the concentration of ODA-RHP solution increased, the blue fluorescence under the irradiation of 365 nm ultraviolet light became stronger. In order to test the UV resistance of ODA-RHP, the ODA-RHP film was placed under an ultraviolet lamp for one week. It was found that the ODA-RHP film still has fluorescence under UV excitation and there was no significant change in the fluorescence lifetime (Fig. 4b and Fig. S12 in ESI), indicating the resistance of UV irradiation of ODA-RHP. It should be noted that the fluorescence of the ODA-RHP film showed detectable red shift, which may be caused by the oxidation of the amine group in the film.

In order to verify the adhesive properties and visualization of ODA-RHP HMA, we used this HMA in the field of cultural relics restoration. The adhesives used in cultural relics restoration must be colorless and transparent. However, the colorless adhesive prevents people from judging the location of the adhesive on the surface of the cultural relic and detecting the repair location. Therefore, it is necessary to find a simple method to determine the position of the adhesive on the surface of the cultural relics, such as fluorescent traces.^[43,44] ODA-RHP HMA can be used in the restoration of cultural relics due to its unique and excellent properties. We found that the repaired bowl could withstand 500 g weight when the bowl was placed in an oven at 100 °C for 6 h, indicating the outstanding performance in cultural relics restoration. Moreover, we placed the repaired ceramic bowl under ultraviolet light, and the cracks can be obviously observed (Fig. 4c). The second principle of cultural relics protection is that the restored cultural relics can be reprocessed, which means that the adhesive is removable. When the adhesive is used for the restoration of cultural relics, it can be dissolved in a green solvent after drying and curing, and can be effectively peeled from the surface of the cultural relics without causing pollution or destruction.^[45,46] Due to the unique hyperbranched

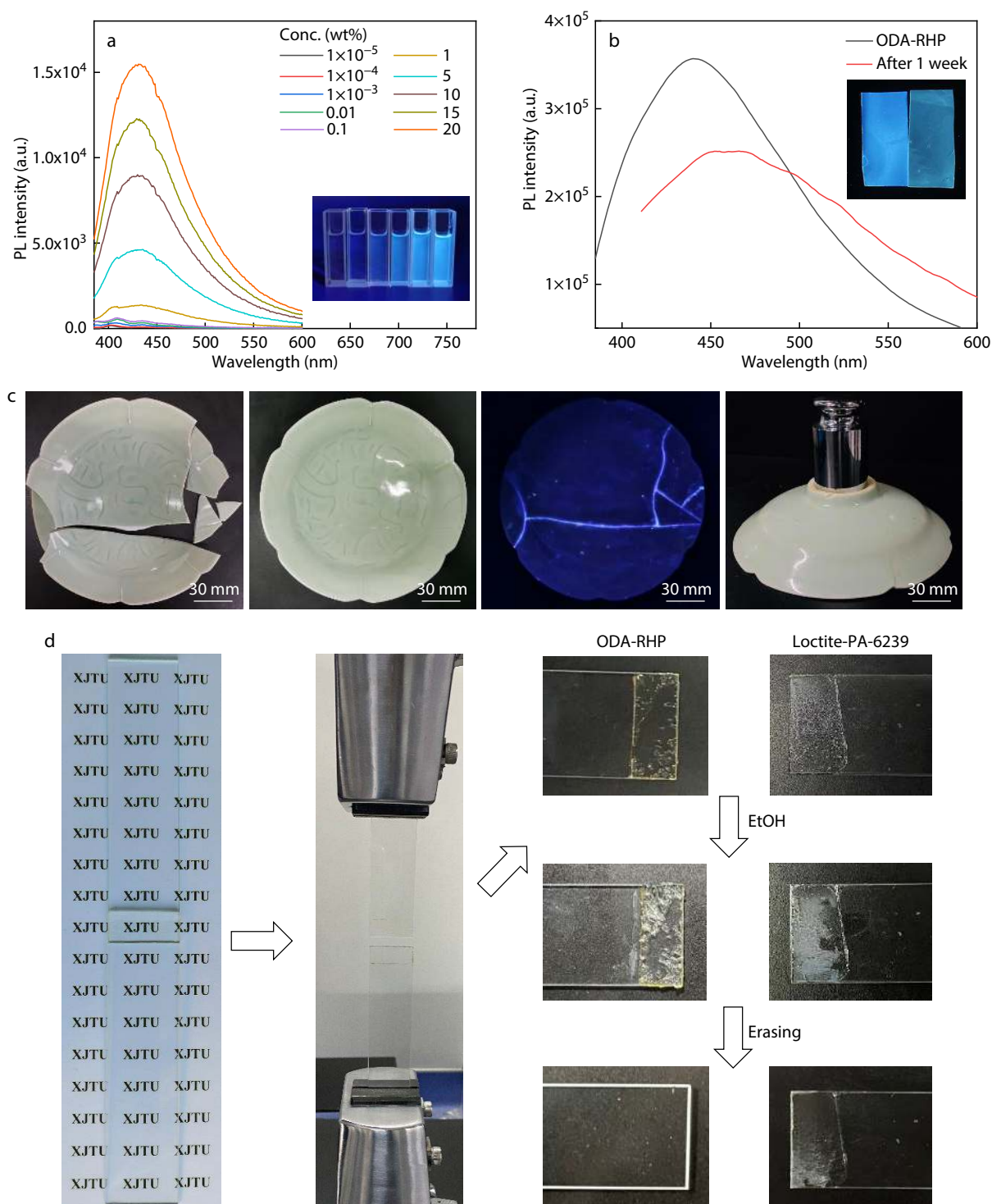


Fig. 4 Fluorescence properties of ODA-RHP. (a) Fluorescence spectra of ODA-RHP in methanol solution. The inset is a photograph of the fluorescence intensity of ODA-RHP solution with increased concentration from left to right; (b) Fluorescence spectra of pristine ODA-RHP and ODA-RHP irradiated by UV lamp (365 nm) for one week. In the inset, the left film is pristine ODA-RHP film, and the right film is ODA-RHP irradiated by UV lamp (365 nm) for one week; (c) Restoration of the ceramic bowl. The broken ceramic bowl was repaired by ODA-RHP, which was placed under UV lamp. The repaired ceramic bowl can withstand 500 g weight after placing in an oven at 100 °C for 6 h; (d) Comparison of the remaining of ODA-RHP HMA and commercial HMA removed by ethanol.

structure of ODA-RHP, it can be dissolved in green solvents such as ethanol, which can be effectively peeled from the bonding surface. As shown in Fig. 4(d), ethanol was dropped

on the remaining ODA-RHP HMA on the bonding surface, and the ODA-RHP HMA film turned into a gel state within 10 s. After gently erasing, the remaining ODA-RHP HMA could be

cleaned up. For comparison, the commercial Loctite-PA-6239 HMA was used, and it was found that it could not be removed after soaking in ethanol for one day. These results demonstrated that ODA-RHP HMA should be a good candidate in the application of cultural relics restoration.

CONCLUSIONS

In summary, a colorless, transparent, removable, and fluorescent polyamide-amine HMA was reported which featured strong adhesive property. The adhesive property of ODA-RHP HMA was superior to those of traditional HMAs, which efficiently bonded a range of substrates including metal, glass, and ceramic. The ODA-RHP HMA could bond materials with short curing time, long storage time, excellent low-temperature resistance, moisture resistant, and reusability. Also, ODA-RHP films exhibited blue luminescence under irradiation of UV light, and the unique hyperbranched structure endowed ODA-RHP HMA with good solubility in ethanol, which can be used to locate the bonding position by fluorescence traces in cultural relics restoration and enable the reprocessing of the restored cultural relics. Overall, ODA-RHP HMA can be used as an effective adhesive in the fields of electronics, machinery, and restoration of cultural relics.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2630-z>.

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