#### Polymer 140 (2018) 150-157

Contents lists available at ScienceDirect

## Polymer

journal homepage: www.elsevier.com/locate/polymer

# NIR induced self-healing electrical conductivity polyurethane/ graphene nanocomposites based on Diels–Alder reaction

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## A R T I C L E I N F O

Article history: Received 10 November 2017 Received in revised form 11 February 2018 Accepted 14 February 2018 Available online 17 February 2018

Keywords: Reduced maleimide functionalization graphene oxide Diels-Alder reaction NIR laser Photo-thermal effect Self-healing

## ABSTRACT

In this work, a crosslinker terminal maleimide groups (EDM) has been synthesized and was used in reactions with the pendant furan groups of polyurethane (PUE) to prepare the self-healing electrically conductive composites based on Diels-Alder reaction, and Ag nanowires (AgNWs) as the conductive network inlaid in the surface layer of the polymer matrix layer. Inspired by the graphene-based materials for its versatility in both material and chemical properties, and we present a new synthetic strategy for the preparation of functional graphene nanosheets with DA group that can be employed in the selfhealing polyurethane system. To our best knowledge, it hasn't been reported yet the structure graphene oxide materials (rmGO) in any systems. The rmGO served as fillers to reinforce the composites and would participated in the DA reactions. The excellent NIR light-induced self-healing property of prepared composites was realized through the photo-thermal effect of rmGO. The composite is capable of both structural and electrical healing via NIR irradiation. The injured samples can be locally repaired with high precision and efficiency without an obvious influence on those uninjured parts. The underlying polymer matrix can reform via the dynamic dissociation/recombination of Diels-Alder bonds to bring the separated areas of the AgNWs layer into contact to restore the conductivity. The NIR light-induced selfhealing electrically conductive composites have wide potential for many fields, e.g., soft robots, flexible devices, and health-monitoring.

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#### 1. Introduction

Electrically conductive materials have been applied in fabrication of various electronics devices, such as energy storage devices [1–4], sensor [5–7], artificial electronic skin [8–10], electrode [11,12] and coating [13]. In practice, it is inevitable electronic devices failure due to mechanical damage. The development of selfhealing conductive materials which improve the reliability, extend the materials lifetime and lower the wasted energy has attracted enormous attention. Many methods have been reported for building up the self-healing conductive materials [14–18]. The Diels-Alder (DA) reaction stand out as a promising strategy to fabricate self-healing conductive materials thanks to highly efficient, simple and repeatedly healed through only the application of heat [19–21]. But the practical application of DA is limited, largely due to the intrinsic issues: in order to heal the materials, requires external heating across the whole materials and can't be specifically localized to the damaged regions to repaire. Therefore, the light show great promise in self-healing materials [22-24], one attractive feature is healed the damage without obvious influence on the uninjured of material. Moreover, it can be precisely controlled by altering the light intensity, exposure time of the light source, and irradiation sites [25,26]. Many photo-thermal conversion agents, e.g. photo-thermal compound [27–29], carbon-based [30,31] and metal nanopartical or nanowires [15,32-34] were used to absorb and converted light energy into heat to induced healing. Both Wang et al. [26] and Shi [35] demonstrated a high NIR light-induced self-healing efficiency of composites based on the thermally reversible DA reaction, the MWCNTs acted as the photothermal conversion agents and cross-linkers. Sun et al. [32] reported silver nanowires (AgNWs) endowed the highly electrically conductive property and the NIR light healability to composites.







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However, the present light triggered self-healing materials had the low self-healing efficiency and mechanical properties.

In general, graphene is an interesting component in self-healing materials as it provides a very efficient photo-thermal effect, which may make it reinforcing and accelerating self-healing [7,36–39]. In this study, low molecular weight polyurethane (PUE) with pendant furan groups and maleimide-terminated compound (EDM) as crosslinker were designed. The structures of PUE and EDM were shown in Scheme S1. The electrically conductive polyurethane composites containing rmGO that are able to be locally healed via the photo-thermal effect was prepared. The rmGO has two effects: as the filler to enhance the mechanical property of systems. Moreover, the photo-thermal effect of rmGO to heal the damaged regions under NIR light irradiation. We chose the AgNWs network with high conductive property [40,41] and NIR photo-thermal effect [32] as the electrically conductive layer, and the AgNWs were partially buried in the surface of self-healing polymer layer. Finally, the investigation demonstrated the composites can realize the structural and electrical local self-healing properties under NIR irradiation without additional processing.

## 1.1. ExperimentalMaterials

4,4'-diphenylmethane diisocyanate (MDI, Aladdin), Polytetrahydrofuran (PTMG,  $M_n = 1000 \text{ g mol}^{-1}$ , Aladdin) was dried in vacuum oven at 100 °C for 2 h. Furfuryl amine, epoxypropane, furan, ethanolamine, maleic anhydride, triethylamine, 3-(aminopropyl) triethoxysilane (APTES), hexamethyldisilazane, Graphite powder (300 mesh), hydrazine hydrate, AgNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were purchased from Aladdin. The chemicals included potassium permanganate (KMnO<sub>4</sub>), concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 98%), hydrochloric acid (HCl, 37%), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), sodium chloride (NaCl), zinc chloride (ZnCl<sub>2</sub>). Dimethylformamide (DMF) and toluene were dehydrated before use, isopropanol (IPA). Other reagents and solvents were used without further purification. The N-(2-Hydroxyethyl)-maleimide (M-E) was prepared according to the report [19], and the structure information was shown in Fig. S1. The compound with maleimide-terminated group (Mi-Si) was synthesized following the literature [42] and the detail structural information was shown in Fig.S2. Graphene oxide (GO) was synthesized by the improved Hummer's method [43]. The maleimide functionalization graphene oxide (mGO) was produced with GO and Mi-Si according to our previous studies [44].

## 1.2. Synthesis of EDM

For the EDM synthesis, both M-E and MDI were used, the detailed process: MDI/DMF (2.5 g/10 ml) was charged into a 250 ml three-necked flask. The M-E/DMF (2.85 g/5 ml) solution was added into the above solution dropwise and the reaction proceeded with magnetic stirring under a nitrogen atmosphere for 5 h at 70 °C. Finally, a yellow solid produce was collected and then dried in vacuum oven for 12 h at 60 °C.

## 1.3. Preparation of rmGO

The mGO/DMF solution (2 mg/ml) was obtained by ultrasonic treatment for 1 h. Next, the hydrazine hydrate was added into the above suspension and then the mixture was heated at 95 °C for 3 h. The final product (rmGO) was washed with deionized water several times, and reserved in DMF.

#### 1.4. Preparation of silver nanowire

The AgNWs were prepared by the modified polyol process [45]. The obtained AgNWs structure information and morphology were shown in Fig. S3.

#### 1.5. Preparation of PU-EDM/rmGO/AgNWs films

The furan pendant polyurethane (PUE) was prepared according to previous report [46]. The self-healing polymer layer was prepared through a simple solution-casting method as follows: the desired amount of rmGO was dispersed in DMF by ultrasonic radiation for about 1 h, and then the required amount of PUE and EDM were added into the rmGO suspension. The mixture was stirred and ultrasonically dispersed for about 30 min. The resulting solution was poured into the glass mould and kept at 65 °C two days to yield PU-EDM/rmGO films. The PU-EDM was also prepared as the control sample by the same procedure but without any rmGO nanosheets.

In a separate procedure, the AgNWs/IPA solution was firstly spray-coated by using an airbrush gun (nozzle diameter: 0.35 mm) on the glass plate to fabricate the AgNWs network coating. The spraying distance was set 10 cm from the surface of the glass. The AgNWs network was annealed at 200 °C for 20 min to produce fusion between the AgNWs. Then the coating on the glass was face-to-face heating pressed with the PU-EDM/rmGO by an iron (the iron was set as 130 °C). After 65 °C one day, the PU-EDM/rmGO/AgNWs was peel off from the glass. We can obtain the final electrically conductive films.

## 1.6. Characterization

FTIR spectra were recorded using a spectrometer (NICOLET 5700, USA) at room temperature. The scan range is from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The <sup>1</sup>HNMR spectra were recorded on a spectrometer (Unity Inova, 400 MHz, USA) using DMSO- $d_6$  as the solvent. Differential scanning calorimetry (DSC) analyses were conducted in a N<sub>2</sub> atmosphere on a thermal analyzer (TA Instruments, Q20, USA) from -60 °C to 180 °C for heating and cooling cycles at a heating rate of 10 °C min<sup>-1</sup>. X-Ray diffraction (XRD) measurements for powder samples were performed on a Bruker diffractometer (Bruker, D8 Advance, Germany) using Cu Ka radiation ( $\lambda = 1.54$  Å) at a scanning rate of 3<sup>min<sup>-1</sup></sup>. A UV-2600 UV-Visible spectrophotometer (Shimadzu Company, Japan) was used to record the absorbance at room temperature with quartz cuvettes with a resolution of 1 nm. Cracks (made by blades) on the surface of samples were observed under a polarizing optical microscope (POM, Leica, DM2500P) equipped with a temperature programmed heating stage to evaluate the healable properties. The temperature was increased at a rate of 10 °C min<sup>-1</sup>. The morphologies of fractured surfaces of films obtained by brittle breakage using liquid nitrogen were studied using scanning electron microscopy (SEM, XL-30 ESEM FEG, FEI Company).

The laser system (LSR808H-5W-FA) used for NIR lightresponsive tests generated NIR light with wavelength of 808 nm. A razor blade was used to make cracks on the sample surface, selfhealing was processed by irradiating under an NIR laser light. The temperature variation was recorded by thermocouple.

The mechanical tensile-stress experiments were measured using a universal testing machine (Instron 121) using ASTM D638 normalized samples as references at a strain rate of 20 mm min<sup>-1</sup>. At least ten samples of each weight fraction were tested at room temperature (25 °C). Tensile strengths were calculated using the integrated area of the stress–strain curves. The self-healing efficiencies can be defined as Eq:

Healing Efficiency (%) = 
$$\frac{\text{Tensile strength}_{(n)cycle}}{\text{Tensile strength}_{original}} \times 100\%$$

Where the Tensile Strength<sub>original</sub> and Tensile Strength  $_{(n)cycle}$  are the average tensile strengths of the original samples and the healed samples, and the n represent the healed times, respectively.

The resistance of samples was tested by using a multimeter.

## 2. Results and discussion

Fabrication of the self-healing polymer layer.

In order to meet the requirement that maintained the dispersibility in solvents and polymer matrix as well as better light absorptivity, the rmGO was prepared using a two-step technique, the detailed fabrication procedures and structure information were given in Scheme S2 and Fig. S4. The Fig. S4 showed a characteristic peaks at 697 cm<sup>-1</sup> due to the maleimide stretching. The maleimide groups can react with furan groups to form DA adduct bond, which promote the compatibility between the rmGO and polymer matrix. Meanwhile, XRD patterns of the rmGO show the broad diffraction peak at  $2\theta = 21.6^{\circ}$ , corresponding to the interlayer spacing of 0.41 nm, compared with GO ( $2\theta = 9.08^{\circ}$ , 0.97 nm), the result suggested the rmGO nanosheets stacked more tightly than the GO owing to the removal of oxygen-containing groups [47], more looser than graphite (0.34 nm) owing to the maleimide groups on the surface of the nanosheets.

The fabrication procedures of composites are schematically illustrated in Scheme 1.

The low molecular weight polyurethane (PUE) and cross-linking agent EDM were used to prepare the self-healing polymer layer. Four different formulations were prepared by using 0.1 wt%, 0.5 wt %, 1 wt% and 2 wt% rmGO in the polymer system (denoted as PU-EDM/rmGO0.1, PU-EDM/rmGO0.5, PU-EDM/rmGO1, PU-EDM/rmGO2).

The DA reaction was confirmed by FTIR spectroscopy, Fig. 1a showed an absorption peak at 697 cm<sup>-1</sup>, which corresponds to characteristic peak of maleimide group of EDM, and the 737 cm<sup>-1</sup> originates from the furan in PUE, and allows for easy identification of these functional groups in the pure polymer and the composites system. It is obvious to find that the characteristic peaks disappeared after the EDM reaction with PUE resulting in DA adduct [48]. The new C=C characteristic peak appeared at 1773 cm<sup>-1</sup> further confirm the DA bonds occurrence [49,50].



Fig. 1. a) FTIR spectra, and b) DSC curves of the PU-EDM and PU-EDM/rmGO nanocomposites.



Scheme 1. Preparation of the PU-EDM/rmGO composites.

In addition, DSC measurements were carried out to monitor the retro DA (rDA) reaction temperature. As is seen from Fig. 1b, the curve shows a very broad endothermic peak from 80 to 140 °C, which reflects an overlay of the glass transition temperature with the breaking processes of the DA bond of the resin. The peaks of the curves appear at 120 °C, we can regard the temperature as the rDA reaction temperature. The thermal reversibility property of DA reaction also was confirmed by DSC in terms of repeated heating/ cooling treatment in Fig S5.

#### 2.1. Morphology and mechanical properties of samples

The composites morphology was monitored using SEM micrographs of the cryogenicaly surface of pure PU-EDM and PU-EDM/ rmGOx samples (Fig. 2). The effect of rmGO on the microstructure of the nanocomposites is very obvious. The pure PU-EDM has the smooth surface (Fig. 2a), as a comparison, the surface of PU-EDM/ rmGOx all show wave-like morphology. And it is no obvious rmGO nanosheets pull-out was observed on the fracture surface of composites. The strong interfacial bonding in the composites could be ascribed two effects: the resudial oxygen groups on the surface of rmGO interacted with the polymer chains via weaker hydrogen bonds. On the other hand, the maleimide groups on the surface of rmGO are expected to react with furan groups of polymer chains. These interaction can significant improved the interfacial compatibility between rmGO and polymer matrix [51].

The mechanical properties of the as-prepared composites with different rmGO loading amounts were measured and illustrated in Fig. 3. It is found that the mechanical properties of the polyurethane system are significantly influenced by the contents of rmGO, DA bonds and the hydrogen bonds during the polyurethane system.

By tuning the weight ration of rmGO, a series of composites with distinct mechanical properties were obtained, the detail results were listed in Table S1. As shown in Fig. 3, it can be seen the incorporation of rmGO can improve the mechanical properties compared to the pure PU-EDM. When increasing the content of



Fig. 2. SEM images of samples with different content rmGO: a) 0 wt%, b) 0.1 wt%, c) 0.5 wt%, d) 1 wt%, e) 2 wt%.



Fig. 3. The stress-strain curves of the PU-EDM/rmGO nanocomposites with various rmGO contents.

rmGO up to 1 wt%, the composite has the highest mechanical strength. These results are mainly due to the strong interactions between rmGO and polymer matrix. In addition, the fine dispersion of rmGO in the polymer matrix lead the efficient load transfer from the polymer matrix to rmGO nanosheets and less stress convergence during the test process. Furthermore, the mechanical strength of sample 2 wt% rmGO loading the mechanical show decreased. This main two reason could be that the higher loading of rmGO, the nanosheets disturb the orientations of polymer chain at high elongations at high loadings [48,52]. On the other hand, the more rmGO may have slight aggregation and decrease the covalently cross-linked DA bonds ratio, the weaker non-covalently cross-linked hydrogen bonds ratio increasing, which leading the mechanical strength decreased and the strain increasing [53].

## 2.2. Photothermal effect and NIR induced self-healing

For realized the remote and local light-induced healing, the local temperature rise is very important, which determined by the photo-thermal effect of the photo-thermal converter [54]. The previous study reported that the weight ratio of photo-thermal converter and the light intensity are two adjustable variables, which could influence the local temperature [54–56]. Therefore, the temperature changes of sample surface with increasing the light intensity and different rmGO content were measured. The temperature of the composites was monitored by a thermocouple, the probe in contact with the films. The results were shown in Fig. 4.

We measured the temperature of samples with and without rmGO after the samples were exposed to NIR (808 nm) for about 2 min to get an equilibrium temperature at different light density. The Fig. 4a shows the relation between the temperature and light density. In our research scope, the balance temperatures as a function of irradiation intensity show a linear manner. The high NIR absorbance of rmGO allowed for effective photo-thermal heating the composites of low rmGO loading (0.1 wt%), the change of temperature for different loading show the similar linear tendency, and the higher slope value is obtained more easily for samples with higher rmGO loading.

Laser density:  $1.0 \text{ W cm}^{-2}$ ; distance from the sample surface to laser: 9 cm.

We also investigated the surface temperature of the samples



**Fig. 4.** Variations of surface temperature of the samples a) with different irradiation intensity, b) with increasing illumination time obtained under the same NIR light conditions.

versus irradiation time with 1.0 W cm<sup>-2</sup> (Fig. 4b). The surface temperature of the PU-EDM/rmGO samples increases with increasing time and reaches a balanced temperature within 1 min in this work.

The rmGO containing composites exhibit a fast temperature rise than pure PU-EDM, which is mainly attributed to the excellent photo-thermal effect of rmGO nanosheets. So that the sample with higher rmGO content obtains higher surface temperature. For example, the temperature of the rmGO 0.1 wt% is increased from room temperature to 100 °C within 1min, and the temperature of the rmGO 2 wt% is increased to 150 °C. We can find the heating rate is higher at the beginning and then declines possibly, this phenomenon maybe due to the fast heat dissipation at higher temperature [57].

As light is turned on, the temperature of the exposed area is increase rapidly, the chain diffusion were accelerated by heating; therefore, we can expected the self-healing efficiency is enhanced by increasing rmGO content. To further examine NIR light healing performance, damage and healing process were carried out on the middle of the dumbbell PU-EDM/rmGO and the control PU-EDM samples with a cut was placed by a razor blade. We exposed these damage samples under the NIR irradiation to heal the damage. The mechanical healing efficiency can be calculated as the ratio of the restored tensile strength to the original tensile strength. Fig. 5 presents a comparison of the mechanical healing efficiencies of a different rmGO mass fraction using ten samples at each composition. The heat treatment samples act as the contrast experiment. The control experiments were processed according to the following process: 100 °C/20 min + 65 °C/48 h.

The healing efficiencies estimated from the experiments are presented in Fig. 5a. All samples show very highly efficient selfhealing properties via heat treatment. However, compared with the other samples, under exposure to NIR irradiation, PU-EDM show relatively low healing efficiency as 62%, this result manifests that the NIR irradiation has a little impact on healing of crack in pure PU-EDM, So, it is obvious that rmGO plays a decisive role in the self-healing process: absorbe light and transform into the heat energy to raise the temperature and heal the crack completely. The weak self-healing ability of PU-EDM could be attributed the movement of the polymer chains to bring the crack surface closer together, the polyurethane chains move quickly during heat treatment, and urethane groups, capable of forming hydrogen bonds. The self-healing mechanism for the systems with rmGO is illustrated in Fig. 5b. After the damage region is exposed to NIR irradiation, the photo-thermal induced heating occurs locally, the more rmGO content can generate more heat energy to raise the temperature, the temperature is above the movement temperature of the polymer chains, and favors polymer chain interdiffusion on the fracture surfaces so that the cracked surface can be



Fig. 5. a) The healing efficiency of different samples, and b) the mechanism of NIR light-induced self-healing.

healed after irradiation. Very important, the higher temperature promoted the DA and rDA reaction to complete the final repair [35,58,59].

Fabrication of conductive healing films.The polymer layer containing 1 wt% of rmGO was chosen to fabricate the self-healing electricity conductive film, because the PU-EDM/rmGO1 had the better mechanical and NIR light-induced-healing properties according to above results. The fabrication procedure is depicted in Scheme 2.

The layer of AgNWs was simply spray-coated from AgNWs/IPA suspension onto the glass. Before transfer, the AgNWs coating was treated at 200 °C for 20 min to enhance the electrically conductivity, the high temperature resulted in a change in the contact resistance between the contacting AgNWs over the large surface area. The weakly bonded AgNWs on the glass were easily transferred to the surface of polymer by a face-to-face heated pressing, as illustrated in Scheme 2. In this case the same temperature and pressure was used, and the increased softness and sticky properties of the polymer matrix in the heated state facilitated wires transferred completely to the polymer without leaving any of them behind on the glass plate [21,60]. The top-view scanning electron microscopy image (Fig. S6a) shows that the AgNWs are compactly stacked to form a mesh-like layer. A cross-sectional SEM image (Fig. S6b) discloses that the AgNWs layer has a thickness of ≈3.97 µm.

Restoration of the electrical conductivity by NIR Light Irradiation.

We investigated the self-healing electrical ability of PU-EDM/ rmGO/AgNWs. First, we observed the change of the conductivity before cut and after healing intuitively. The Fig. 6 a shows the process, the film was connected in a tandem circuit with a bulb was employed for monitoring the conductive behavior of the film. The film was cut with a razor blade, the lighted bulb was immediately extinguished (Fig. 6 a2). The film was exposed upon NIR irradiation within 5min (808 nm, 1 W cm $^{-2}$ ), the bulb would light up again as that of the original film (Fig. 6 a3) [61], respectively. Furthermore, we can find a residual valley on the surface of composites after being healed (Fig. S7), this the reason that the resistance can't recover the original value [60], which can be explained by following factors: although the underlying PU-EDM/rmGO film healed well, it was difficult for the AgNWs network to reconnect during each cycle owing to the mismatch of the separated polymer surfaces. A large surface mismatch could make it difficult to rejoin the scratched film [21,60].

The healable property of the composites is important for the durability of functional devices and structures employing the conductor. To investigate the recovery of the conductivity upon NIR irradiation, we quantitatively characterized the resistance change. The samples were repeatedly scratched at the same location and the healing process was completed by 808 nm NIR irradiation.



Scheme 2. Schematic of the fabrication of PU-EDM/rmGO/AgNWs film.



**Fig. 6.** The self-healing of electrical conductivity of the as-prepared composites films, a) circuit schematic with a bulb in series with the film and healing process. a1) the original; a2) after cutting; a3) light healing of the film. b) Measured resistance after up to three cycles of repeated scratching and healing.

(5min, 1 W cm<sup>-2</sup>). The nanocomposites show remarkable light healability under the NIR. The measured resistances are summarized in Fig. 6b. The resistance of specimen with initial resistance of 2.23  $\Omega$  increased to  $10.02 \times 10^7 \Omega$  after each crack formation. The resistance recovered to 3.24, 5.23, and 110.24  $\Omega$  via 5 min of NIR irradiation at 1 W cm<sup>-2</sup> after the first, second, and third cut, respectively.

The composite shows electrical healed with the aid of NIR irradiation. The healing property should be resultant from two healing processes: the healing of the underlying polymer layer and the reformation of the AgNWs layer. With the NIR irradiation, the rmGO can continue to effectively convert the light energy into thermal energy, heating the polymer layer. In this way, the polymer layer becomes soft, and the polymer nearby the damaged region is driven by the reduction of its surface tension to flow into the damaged area to fill the gap. Because of the strong adhesion between the AgNWs layer and the polymer layer, the flow of the polymer layer causes the separated AgNWs layers to move toward each other. During this process, the damaged region of the film disappears or distinctly narrowed, and the polymer layer is covered by the AgNWs layer. Therefore, the conductivity of the damaged film is restored [15,17].

156

## 3. Conclusions

In summary, the NIR light-induced self-healing electrically conductive composite based on the dynamic covalent Diels-Alder reaction has been successfully developed. The introduction of the rmGO to the polymer matrix and AgNWs network inlaid in the polymer matrix layer endowed the excellent NIR light-responsive property and conductivity. In addition, the maleimide groups on the surface of rmGO improved compatibility with the polymer matrix and enhanced mechanical property of the composites compared with the similar reports. We also research the influence of rmGO contnet on the photothermal effect and self-healing property of the nanocomposites. The conductivity can be recovered with a 808 nm NIR irradiation. For certain application, such a self-healing property can remarkably extended the lifetime of electronic devices, and may provide new method for the design and fabrication of various next-generation self-healing electronic devices

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.02.036.

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