Composites Science and Technology 133 (2016) 165–172

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Photothermally induced scratch healing effects of thermoplastic nanocomposites with gold nanoparticles

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ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form
15 July 2016
Accepted 30 July 2016
Available online 1 August 2016

Keywords:
Coating
Self-healing
Gold nanoparticles
Photothermal effects

ABSTRACT

A novel method for providing thermoplastic coatings with light-triggered self-healing ability is reported. Normal thermoplastic coatings can be healed efficiently via local heating generated by photothermal effect of gold nanoparticles (Au NPs). Small amounts of Au NPs were successfully dispersed into the coatings. Once the scratch occurred in the coating surface, a laser could be used to illuminate Au NPs to generate a large amount of heat which dramatically increased the local temperature through the photothermal effect. It would melt the polymer and form local deformation to merge the scratch efficiently. It had been confirmed that the coating containing Au NPs had the healing ability. After healing, the surface morphology and the mechanical property were recovered. The mechanism of the healing was also investigated and it was found that the Au NPs content and irradiation intensity played the key roles in the healing process. Through adjusting these two elements, the maximum temperature rise could achieve 225.5 °C. Healing tests were carried out on multiple types of thermoplastic coatings (PAA, PVAc, PS and TPU) and repeated healing was also achieved.

1. Introduction

Nowadays, polymer coatings are widely used for decoration and surface protection, which has become an indispensible element for manufacturing industry, especially in the fields of automobile and electronic manufacturing. Polymer coating not only provides a glazed surface but also creates a barrier between the substrate and corrosive media. However, the protection is not constant. In the using process, scratches will generate gradually under weathering and mechanical impact, which will dramatically influence the protecting and decorating performance of coating. Since the creation of a perfect coating with permanent appearance seems to be impossible, the concept of making self-healing coatings becomes one of the main approaches.

Since the report of microcapsule-based self-healing coatings by Cho and coworkers [1], a large number of similar approaches have been presented [2–5]. In their studies, microcapsule-based coatings with significant self-healing capability were manifested from damage. However, the damage could be healed only once at a same spot and the synthesis of these self-healing materials was complicated. Apart from the capsule based self-healing method, stimuli response self-healing was another effective strategy. In this healing strategy, instead of introducing cohering materials, healing process was based on diffusion and reconnection of the fracture surface polymer chains, which was typically initiated by the internal or external stimuli, such as heat [6], pH [7] or light [8–10]. However, the molecule movement of long polymeric chains is strongly limited. To increase the mobility, one traditional method is to design some special molecule chains. The disadvantage of the method is that the material is restricted to soft polymers, such as elastomers, hydrogels or polymers with low glass transition temperature (T_g) [11–14]. Nonetheless, for all kinds of thermoplastics, there is a simple way to make molecule to be extremely active and enable it to realign, which is calefaction. High temperature can lead the fracture to melt, therefore the scratch will merge. However, heating polymer is a tough process and it seems to be inappropriate to repair the scratch by heating the whole structure. The best way would be heating the local site to achieve fast melting and obtain reconnection in the scratch area.

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http://dx.doi.org/10.1016/j.compscitech.2016.07.032
0266-3538/

Recent studies have suggested that gold nanoparticles (Au NPs) are an ideal tool for local heating, which has an extraordinary property of photothermal effect. When Au NPs interact with the incident light with the wavelength near the surface plasmon resonance (SPR) absorption, the abundant outer electrons will vibrate fiercely and the temperature of the particles raise significantly, thus heating the local environment [15]. Consequently, the photothermal effect of Au NPs is emerging as a powerful tool in the manipulation of nanoscale thermally activated processes, which has been utilized for photothermal cancer therapy [16–19], chemical deposition [20,21], nanolithography [22,23] and nanoscale patterning [24,25]. In the recent published works, the photothermal effect of Au NPs was employed to achieve local heating, which could quickly heat the matrix spatially and leave the remainder unchanged [26–34], indicating that Au NPs was a promising candidate for self-healing of polymer coating.

In this paper, a little amount of Au NPs was introduced into thermoplastic coatings to provide self-healing ability. A laser was used to trigger the healing effect. The healing process was spatially flexible and remote controllable. The influences of some key factors, such as Au NPs content and laser irradiation intensity, were investigated and the healing mechanism was also discussed.

2. Material and methods

2.1. Material

Chlorauric acid ($HAuCl_4$) and oleylamine were purchased from J&K Chemical Ltd. Acrylic resin (PAA) was purchased from Yangzhou municipal Xing Resin Co., Ltd. Polystyrene (PS), methanol and N,N-Dimethylformamide (DMF) were purchased from Aladdin. Toluene was purchased from Sinopharm Chemical Reagent Co., Ltd. Polyvinyl acetate (PVAc) was purchased from Shanghai Macklin Biochemical Co., Ltd. Thermoplastic polyurethane (TPU) was purchased from Dongguan Huahong Engineering Plastic Co., Ltd. All chemical reagents were used without further purification.

2.2. Fabrication of Au NPs

Oleylamine-stabilized Au NPs were synthesized by following Liu's method [35]. Solid chlorauric acid (80 mg) was dissolved in oleylamine (20 mL) in a three-necked flask equipped with a condenser and a stir bar. The solution was heated to 150 °C under flowing N_2 and kept at this condition for 1 h. After reaction, the Au NPs were purified by precipitation with methanol, followed by centrifugation and washing with methanol, and then dispersed in toluene (40 mL).

2.3. Preparation of polymer/gold nanocomposite coatings

The Au NPs-loaded nanocomposites were prepared through solution mixing method. Solid PAA resin and toluene were firstly added into a flat bottom flask to prepare the polymer solution at 80–90 °C. Then a desired amount of oleylamine-stabilized Au NPs solution was introduced into the polymer solution. The mixture was mixed with a magnetic stirrer for 5 min and then was sonicated for 10 min to further disperse the Au NPs. Finally, the final solution was cast onto the clean steel sheets or coverslips and dried in an oven. The initial temperature was adjusted to 80 °C and lasted for 20 min. The temperature was then gradually raised to 120 °C within 60 min to completely evaporate the solvent. The final thickness of the coating was controlled around 35 μm. In addition, following the same procedures and under the same conditions, replacing PAA with PS, PVAc and TPU (TPU was dissolved in DMF), various nanocomposite coatings were prepared.

2.4. Temperature monitoring of photothermal effect

The photothermal effect of Au NPs was investigated through testing the local temperature of PAA/Au NPs coating under irradiation of a 532 nm continuous-wave diode laser with the power of 400 mW. A tiny thermocouple was buried in the coating to measure the local temperature of the irradiated region. A series of PAA/Au NPs coatings were irradiated by the laser with different irradiation intensity. The laser beam was avoided from hitting the thermocouple directly, but was kept as close to the thermocouple as possible. The temperature change was recorded by a computer every 0.5 s until it reached a steady state.

2.5. Healing process

In the healing process, the scratched coating samples loaded with Au NPs at various low contents (0.005 wt%, 0.01 wt%, 0.02 wt% and 0.04 wt%) were irradiated by the 532 nm continuous-wave diode laser with the power of 400 mW, whose irradiation intensity can vary from 50 to 300 W/cm^2 by changing the beam size. The scratches before and after irradiation were checked under an optical microscope. The healing effect was observed through SEM and AFM test. The healing efficiency was evaluated through tensile test.

3. Result and discussion

3.1. Photothermal healing of Au NPs loaded coating

The surface morphologies of the scratched region in pure PAA and PAA/Au NPs coatings after irradiation healing are shown in Fig. 1a, b. After irradiation, there is still visible scratch on pure PAA coating. However, no obvious scratch exists on the PAA/Au NPs coating, which means that the scratch has already been markedly healed. Obviously, the introduction of Au NPs endowed the resin matrix with healing ability.

Fig. 2a, b shows the optical images of the as-prepared PAA/Au NPs coating casted on a coverslip and the same one damaged by 1500-grit sandpaper, whose center region was then healed, as shown in Fig. 2c. After healing, the smoothness and the transmittance of the healed region recover the state before damage, and the scratches are totally visually unobservable. The healing process of the coatings (Fig. 2a–c) was further confirmed by the change of root-mean-square (RMS) roughness characterized by AFM. The as-prepared PAA/Au NPs coating has a roughness of 27.365 nm. After damage, the RMS roughness increases to 709.42 nm, and then dramatically decreases to 41.220 nm after photothermal healing, approaching to that of the as-prepared coating. Additionally, to evaluate the healing efficiency, tensile test was carried out to evaluate the healing efficiency (the detail of which is given as Supporting Information).

It is clearly that not only the morphology but also the mechanical properties of the nanocomposite coating are recovered, indicating that the healing method could perfectly repair the damaged coating by taking the advantage of the photothermal effect of Au NPs. Fig. 3 shows the schematic of the healing process. The Au NPs dispersed in the coating serve as unique local nanoheaters. Once the coating is scratched, a laser could be used to illuminate the scratch to dramatically raise the local temperature, which would melt the polymer, so that the polymer chains in the irradiated region could diffuse across the scratch. While the polymer is heated by Au NPs, there would be volume expansion in the local irradiated area. However, the expansion is restricted by the surrounding cold polymer. Thereby, an interior stress towards the scratch forms, which pushes the two sides of the scratch to