

Preparation of acrylate copolymer modified by TiO₂ nanoparticles with excellent photo-oxidative stability for application in ancient ivory conservation

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ABSTRACT: In this work, acrylate copolymer has been fabricated by graft copolymerization of acrylate monomer (EMA:EA is 70:30) with functional TiO₂ nanoparticles, which was surface-modified by the silane coupling agent methacryloxy propyl trimethoxyl silane (KH570) to attach active ends. The structure and properties of the copolymer were characterized by FT-IR, FE-SEM, differential scanning calorimetry, thermogravimetric analysis, ultraviolet-visible spectra, and discoloration. Characterization revealed that functional TiO₂ particles were grafted onto the chain of the acrylate copolymer and the acrylate copolymer showed excellent photo-oxidative stability and transparency. The acrylate copolymer was applied to protect and consolidate ancient ivory by surface coating without destruction of chemical structure. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43291.

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INTRODUCTION

Acrylate copolymers have been of continuous research interest since they have many useful and unique properties,^{1–4} including optical clarity and superior mechanical strength, adhesion, and chemical stability, that make them valuable in many important fields such as paints, surface coatings, and cultural heritage conservation materials.^{5–13} An example is Paraloid-B72, which is the copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) in the molar ratio 70:30.¹⁴ Rossi *et al.* assessed the consolidation of cremated bone with B72 or polyvinyl butyral (B98) using simple brushing and immersion techniques.¹⁵ Lucía and coworkers reported that B72 dissolved in toluene and acetone solution (1:1) was applied to conservation of a human mandible from the Pleistocene site of Gran Dolina (Sierra de Atapuerca, Spain).¹⁶ Unfortunately, many papers have reported photo-oxidative activity of acrylate copolymer, which has been found to cause yellowing and cracking because of degradation brought about by oxidation and chain scission reactions.^{1,5}

Research on the photo-oxidative stability of acrylate copolymers in recent decades has generally been focused on the use of functional materials with ultraviolet shielding for blending with the polymer, where the functional material dispersed around the

polymer absorbs the ultraviolet light, thus preventing degradation.^{10,17–19} Nano-TiO₂, for instance, is known to have high photocatalytic activity because of its large specific surface area and high photosensitivity.^{20–22} However, the nano-TiO₂, which has high surface energy, is easy to agglomerate and difficult to disperse.²³ Many researchers use silane coupling agents and surfactants to improve its dispersion, although it is difficult to balance the dosage of TiO₂ with transparency, and thus the materials may turn white after long-term use.⁷

In this study, acrylate copolymer was prepared by graft-copolymerization of acrylate monomer (EMA:EA is 70:30) with functional TiO₂. The functional TiO₂ was modified by the silane coupling agent methacryloxy propyl trimethoxyl silane (KH570) to attach active ends. Subsequently, the resulting acrylate copolymer was used as a conservation material to protect and consolidate archaeological specimens (such as ancient ivory) by surface coating. The structure and properties of the copolymer were characterized by FT-IR, FE-SEM, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), ultraviolet-visible spectra (UV-vis), and discoloration. The functional TiO₂ was speculated to be uniformly grafted onto the acrylate copolymer chain,^{24,25} as shown in Figure 1, which ensured the acrylate

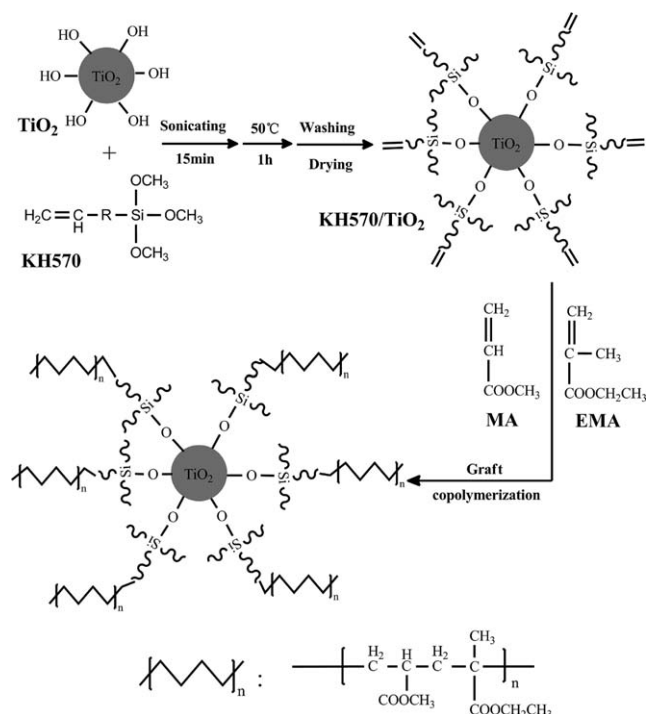


Figure 1. Preparation of acrylate copolymer modified with functional TiO₂.

copolymer has high ultraviolet absorption and excellent photo-oxidative stability. Instead of conventional physical mixing method, chemical graft modification could avoid aggregation of nano-TiO₂ on a large scale to keep the acrylate copolymer transparent and have no effects on appearance of ancient ivory. In addition, the introduction of nano-TiO₂ could improve the weatherability and durability, which has high practical value in application of bone relics conservation.

Materials

Functional nano-TiO₂ (KH570/TiO₂) coated with methacryloxy propyl trimethoxyl silane, a mixture of 80% anatase and 20% rutile with an average surface area 100 m²/g and an average diameter of about 50 nm was obtained from Hang Zhou Wan Jing New Material (Hangzhou, China), Azobisisobutyronitrile (AIBN, 99%, Sigma Aldrich), EMA (99%, Sigma Aldrich), and MA (99%, Sigma Aldrich).

Modification of Acrylate Copolymer

The acrylate copolymer was prepared via *in situ* polymerization. Different quantities of modified nano-TiO₂, as shown in Table I, were added into a 250 mL four-necked flask charged with 100 mL ethyl acetate. The mixture was then sonicated for 40 min, and the flask was immediately equipped with a reflux con-

denser and a mechanical stirrer. The mixture of EMA-MA (EMA:27.5 mL, MA:13.5 mL) and initiator (AIBN:0.1136 g, weight concentration:ca. 0.5%) were slowly added dropwise to the suspension over 30 min under a nitrogen atmosphere, with vigorous stirring. This was continued at 82°C for 7.5 h to ensure complete reaction. Subsequently, the resulting ethyl acetate solution was dropped into 1000 mL petroleum ether to remove the residual monomer of EMA-MA and the precipitation was collected. The purification process was repeated three times. Finally the acrylate copolymer (KH570/TiO₂-B72) was obtained by vacuum drying the precipitation at 50°C for 12 h.

Preparation of Acrylate Copolymer Films

The acrylate copolymer was dissolved in mixed solutions of ethanol and acetone (weight concentration of modified copolymer:ca. 15%), and then 10.00 mL volumes of the mixed solutions were transferred to standard molds to form thin films measuring 50 × 40 mm. The formed films were then dried under vacuum at 60°C for 4 h. The thickness of the films was 260–270 μm.

Conservation of Ancient Ivory

The ancient ivory was provided by Shanghai Museum, unearthed from the M207 tombs of Fuquanshan site (Shanghai, China). Before the conservation experiment, the ancient ivory sample was repeatedly washed with deionized water and acetone, and then dried naturally at room temperature. Subsequently, the cleaned ancient ivory sample was coated with 7.5 wt %²⁶ KH570/TiO₂-B72 acetone solution by brushing three times, dried at 33°C, and placed in a desiccator.

Characterization

The attenuated total reflectance (ATR) spectra of the acrylate copolymer (0.10 wt % TiO₂) were recorded on a Fourier transform infrared spectroscopy spectrometer (Nicolet 380, Nexus, America) with a resolution of 4 cm⁻¹.

The photo-degradation of acrylate copolymer films was measured by the absorption of the carbonyl stretching vibration, calculated as follows:

$$I_{\text{wn}} = (A_{\text{wn}})_t / (A_{\text{wn}})_0$$

where A is the absorbance of the carbonyl stretching vibration ($\text{wn} = 1730 \text{ cm}^{-1}$) measured at wave number wn . The subscripts t and 0 refer to a generic aging time t and to the unaged sample, respectively.

The UV-vis of the acrylate copolymer films were acquired with an ultraviolet-visible spectrophotometer (UV1900PPC, Shanghai Jinhong, China).

The thermal analyses of the acrylate copolymer (0.10 wt % TiO₂) were performed on a DSC (DSC Q20, TA, American)

Table I. The Mass of Nano-TiO₂ in Different Resulting Samples

Samples (TiO ₂ wt %)	0.01%	0.03%	0.05%	0.07%	0.10%	0.30%	0.50%
TiO ₂ /g	0.004	0.011	0.019	0.027	0.038	0.114	0.190

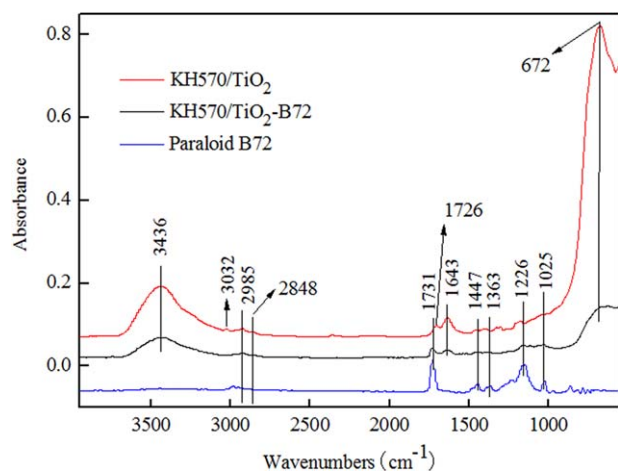


Figure 2. The FT-IR spectrum of samples (Paraloid B72, KH570/TiO₂ and KH570/TiO₂-B72). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and a thermogravimetric analyzer (TGA TA2910, TA, American) under a nitrogen atmosphere at a heating or cooling rate of 20 °C/min.

The morphology of the acrylate copolymer film was characterized using a scanning electronic microscope (FE-SEM, SU-8000, Hitachi, Japan).

Photochemical aging was carried out using a Suntest CPS light fastness testing chamber equipped with a Xenon lamp source filtered for $\lambda < 295$ nm, and having a constant irradiation at a power of 765 W/m². The distance between the lamp and film was 20 mm. Color measurements were performed with a tristimulus colorimeter by using the standard EN 15886:2010. The color coordinates L^* , a^* , and b^* were measured based on the CIELAB (1976) system; with these values, the total color difference (ΔE^*_{ab}) was calculated. All three coordinates were measured, and b^* (measuring the yellow to blue scale) was selected as giving the best indication of yellowing. The color changes during photodegradation were characterized by a Data Color 650 machine that was set to measure an area of 3 mm; each measurement was repeated six times and the average value was recorded. Results were expressed using the CIELAB 1976 color system (L^* , a^* , b^*) under the standard illuminant D65 and using the 10° standard observer. The device was calibrated against a white working standard supplied with the instrument.

RESULTS AND DISCUSSION

Chemical Structure Characterization of Acrylate Copolymer

The chemical structure of the copolymer was analyzed using FTIR-ATR by comparing the original and the modified acrylate copolymer. The spectra of KH570/TiO₂, Paraloid-B72 and modified acrylate copolymer (0.10 wt % TiO₂) are shown in Figure 2. When the functional nano-TiO₂ was added, the C=C group absorption (3032 cm⁻¹) disappeared, and the strong absorption band at 672 cm⁻¹, assigned to the Ti-O group,²⁷ indicating that the functional nano-TiO₂ was grafted to the acrylate monomer, producing the acrylate copolymer. After

modification with functional nano-TiO₂, there was a blue shift in the carboxylic C=O absorption peak of the acrylate copolymer from 1726 to 1731 cm⁻¹. The relative amount of Paraloid-B72 decreased because of the addition of KH570/TiO₂. Therefore, the strength of Paraloid-B72 original absorption bands (such as the bands at 1731 and 1226 cm⁻¹) was weakened¹⁷. The bound water of functional nano-TiO₂ was recognized by broad bands at about 3436 and 1643 cm⁻¹. Absorption bands in the range of 2800–3000 cm⁻¹ were also observed in the spectrum, corresponding to C–H stretching mode peaks. The sharp peaks appearing at about 2985 cm⁻¹ $\nu_2(\text{CH}_3)$ and 2848 cm⁻¹ $\nu_2(\text{CH}_2)$ indicated the presence of the acrylate copolymer groups.

Influence of Functional TiO₂ on the Optical Properties of Acrylate Copolymer

There was clearly an influence of the quantity of the added functional TiO₂ on the optical properties of acrylate copolymer. Figures 3 and 4 show that the absorbance and photo-oxidative stability of the acrylate copolymer increased gradually with the increase in the quantity of functional TiO₂ (299 and 324 nm are the characteristic absorption wavelengths of rutile and anatase titanium dioxide). On the other hand, the transmittance of acrylate copolymer film was reduced gradually with the increase in the quantity of the functional TiO₂. Thus, the optimum dosage of the functional TiO₂ when considering the ultraviolet absorption and transmittance of the film was 0.1 wt %, where the maximum absorption was 0.2862 and 0.6194 at 299 and 324 nm,²⁸ respectively. The average transmittance was more than 78.8% in the range of 400–800 nm.

Influence of Functional TiO₂ on the Thermal Properties of Acrylate Copolymer

The thermal stability of the modified and unmodified acrylate copolymer was studied using TGA, as shown in Figure 5. The weight loss of the samples started at about 280 °C and stopped at about 450 °C. The curves presented only a one-stage

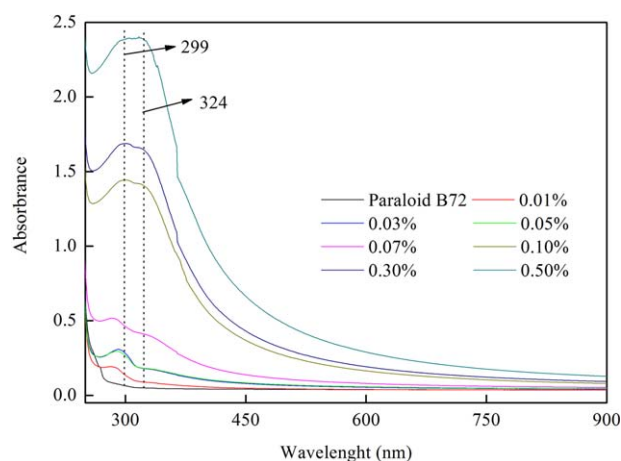


Figure 3. The UV spectrum of acrylate copolymer with different quantities of TiO₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

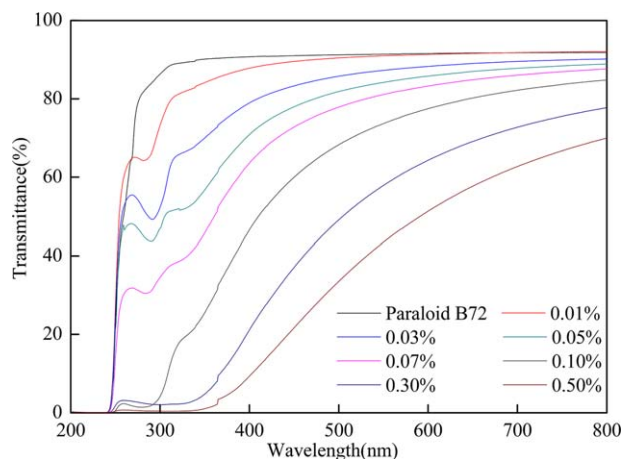


Figure 4. The transmittance of acrylate copolymer with different quantities of TiO_2 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation process, showing that there was no effect of the functional TiO_2 on the thermal stability of the acrylate copolymer.

The heat absorption conditions of acrylate copolymer (0.10 wt % TiO_2) were determined using DSC, as shown in Figure 6. It is apparent that the motion of the acrylate copolymer chains was restricted with the addition of functional TiO_2 , so the glass transition temperature (T_g) increased from 36.06 °C to 36.35 °C, and the heat of the chain unit motions increased from 0.3347 to 0.3744 J/g. The glass transition temperature of KH570/ TiO_2 -B72 without division showed that the modification of TiO_2 did not conflict with the graft copolymerization. This confirms that the functional TiO_2 were grafted onto the macromolecular chains.

Microstructure Characterization of Acrylate Copolymer

The morphology and microstructure of acrylate copolymer were studied by Field-Emission scanning electronic microscopy (SEM). Figure 7 shows the SEM images. The functional TiO_2

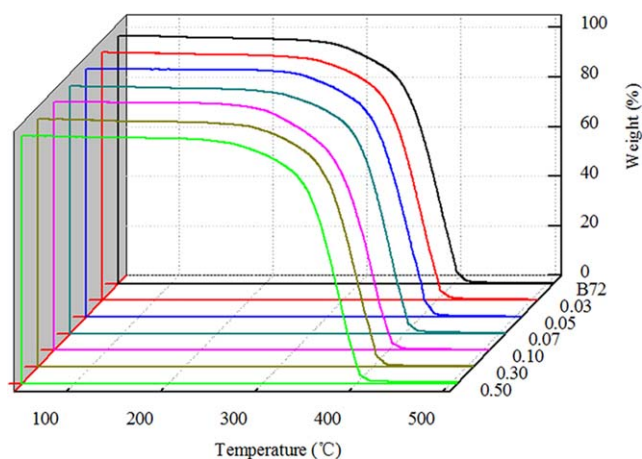


Figure 5. The TGA spectrum of acrylate copolymer with different quantities of TiO_2 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

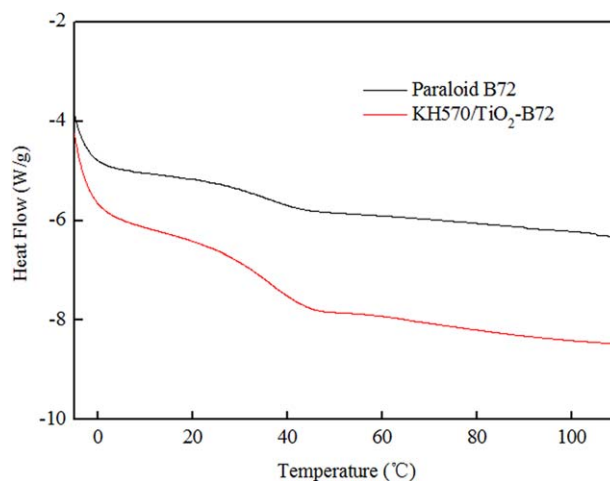


Figure 6. The DSC of samples (Paraloid B72 and KH570/ TiO_2 -B72). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanoparticles were grafted onto the macromolecular chains, and most of them were uniformly dispersed, with part of them aggregation in partial region. Most of the functional TiO_2 appears to be grafted onto the polymer chains of acrylate

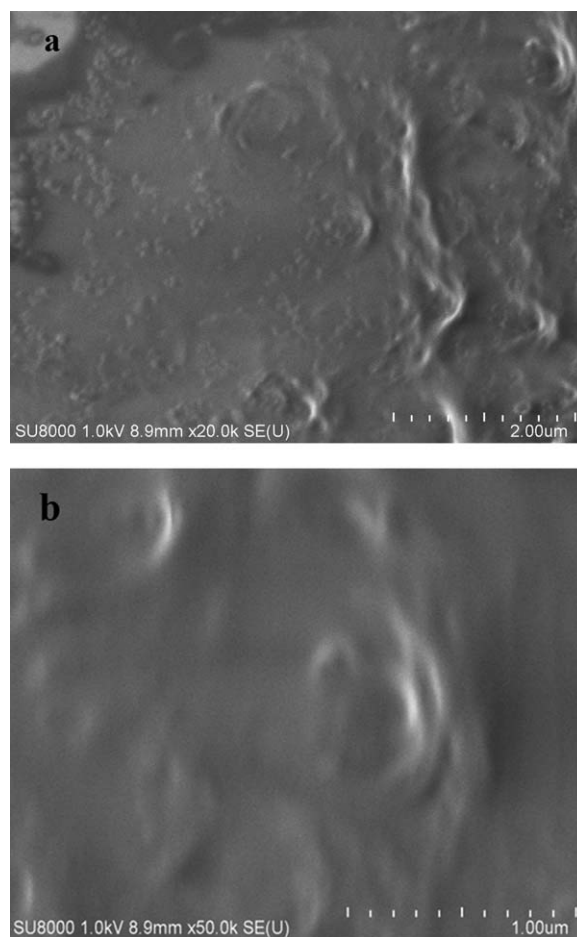


Figure 7. The SEM of acrylate copolymer films.

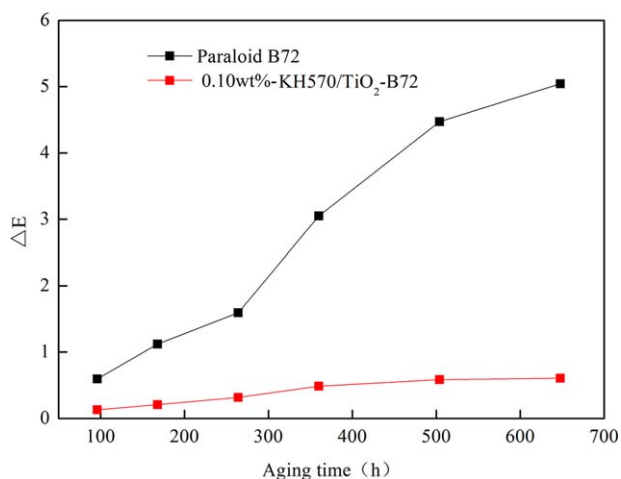


Figure 8. The color change of acrylate copolymer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymer, forming a ball coated by acrylate copolymer.²⁹ The balls are uniformly dispersed in acrylate copolymer.

Photo-Oxidative Stability of Acrylate Copolymer

The change in color of acrylate copolymer films was because of the photo-oxidative processes and the consequent formation of new chromophores.^{1,2,5,7,30,31} Figure 8 shows the color variations of acrylate copolymer films with and without added functional TiO₂ (0.10 wt %) upon exposure to ultraviolet radiation. It is clear that the color changes of the film without TiO₂ increased with increased aging time, but the color variations of the film with added functional TiO₂ were less than 1 up to the maximum aging time, 648 h under ultraviolet irradiation, which has an advantage over other acrylic copolymer coating materials.^{5,7,8} The added functional TiO₂ improved the acrylate copolymer photo-oxidative stability, as demonstrated also by the slopes of the curves of Figure 9.

The influence of the added functional TiO₂ on the chemical stability of the acrylate copolymer was measured by FTIR spectroscopy.

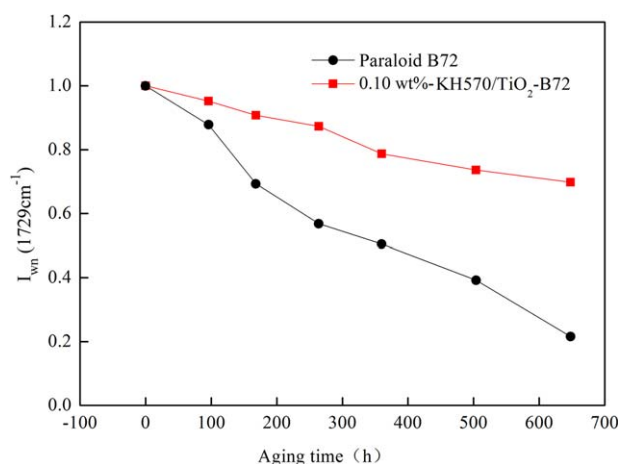


Figure 9. The ATR (1730 cm⁻¹) of acrylate copolymer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

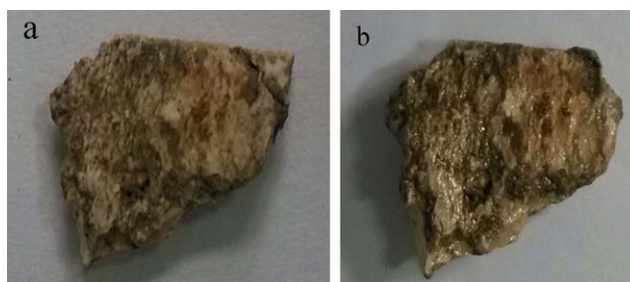


Figure 10. The photos of ancient ivory: (a) before conservation and (b) after conservation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copy. The photo-oxidative mechanisms of Paraloid-B72 have been reported in a number of articles.^{1,2,5} The acrylate copolymer undergoes oxidation and chain scission reactions during photo-oxidative reaction.^{1,5,7} Figure 9 presents the variation of the carbonyl absorption (1730 cm⁻¹): when the acrylate groups were damaged, they formed carboxylic acids (1710 cm⁻¹) and γ -lactones (1780 cm⁻¹). When the functional TiO₂ units were

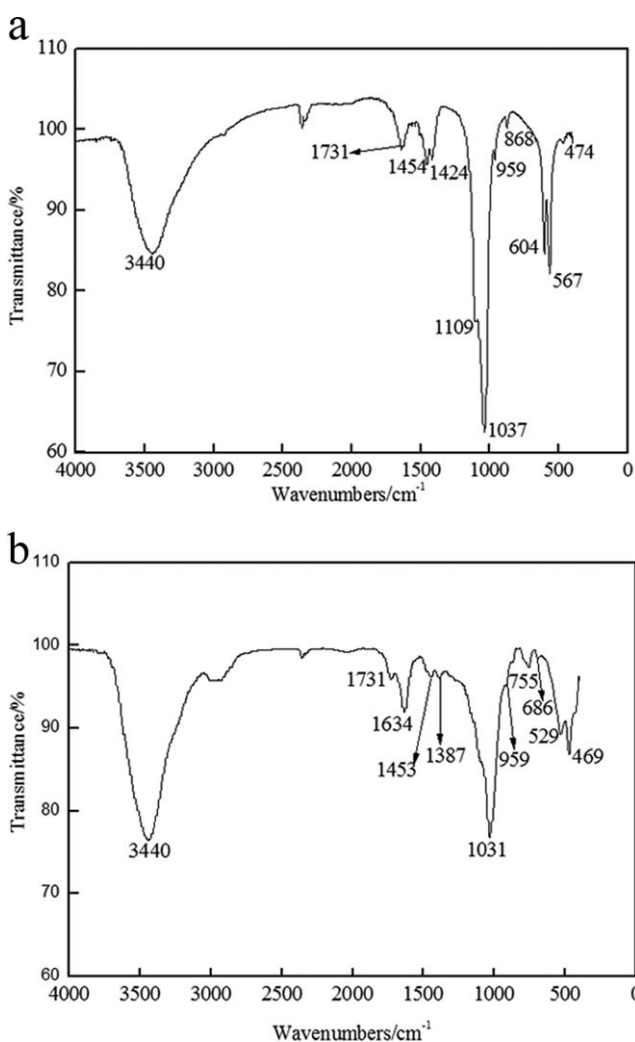


Figure 11. The FT-IR spectrum of ancient ivory (1 cm deep): (a) before conservation and (b) after conservation.

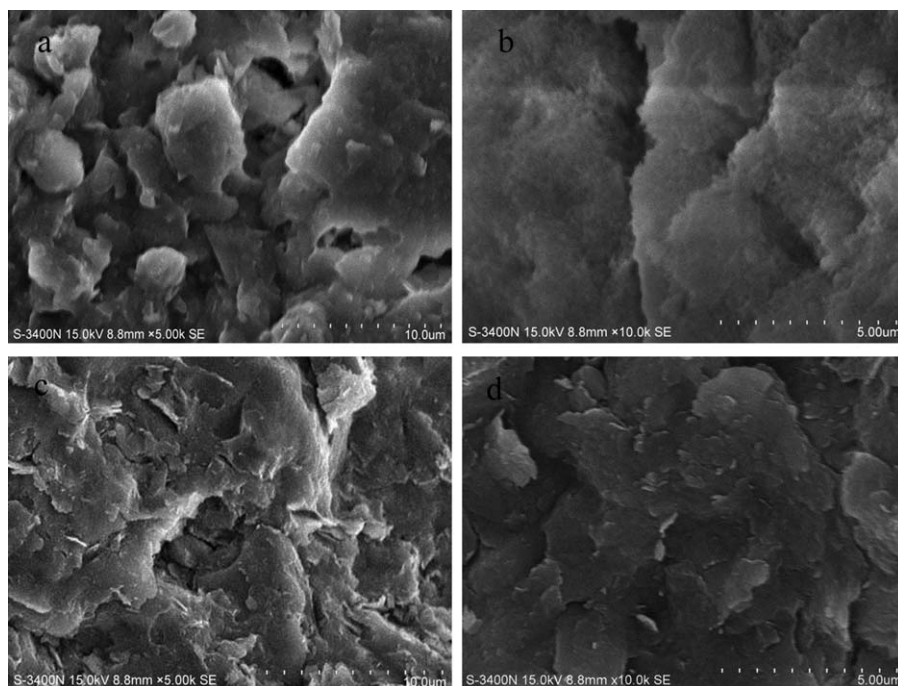


Figure 12. SEM images of ancient ivory: (a, b) before conservation; and (c, d) after conservation.

added to the acrylate copolymer film, the grafted functional TiO_2 slowed down the oxidation reactions and stopped the chain scission reactions, which improved the photo-oxidative stability of the acrylate copolymer as illustrated in Figure 9.

Conservation Performance on Ancient Ivory

About 7.5 wt % KH570/ TiO_2 -B72 acetone solution was brushed onto the surface of ancient ivory sample for conservation. Figure 10 shows the photos of ancient ivory before and after conservation. The grain of the ancient ivory sample was still clearly visible after conservation, which shows that the conservation had no effect on the ornamental value of ancient ivory.

The functional groups of ancient ivory before conservation were identified by FTIR spectroscopy, shown in Figure 11(a). The bands at 1037 and 604 cm^{-1} were assigned to asymmetric stretching vibration of PO_4^{3-} , and the bands at 1424 and 1454 cm^{-1} were attributed to C-O vibrations of CO_3^{2-} , which was present because there is hydroxyapatite in ivory.³² The characteristic absorption peaks (1663 , 1558 , and 1240 cm^{-1}) of collagen were not found in FTIR spectrum, which showed that the collagen has been destroyed completely during the long burial. Figure 11(b) presents the FTIR spectrum of ancient ivory (1 cm deep under the surface) after conservation. Compared with Figure 11(a), there was little difference in Figure 11(b) except the band at 686 cm^{-1} , which was assigned to Ti-O-Ti vibrations. It shows that the KH570/ TiO_2 -B72 penetrated to the interior of the ancient ivory where there was no destruction or change of chemical structure.

The morphological characteristics of ancient ivory before and after conservation were investigated by SEM (Figure 12). As shown in Figure 12(a,b), there were many inhomogeneous and discontinuous pores with partial collapse and impurities in ancient ivory before conservation. The pore diameter was about

$0.33\text{--}3.6\text{ }\mu\text{m}$. After conservation as shown in Figure 12(c,d), these inhomogeneous and discontinuous pores were filled with KH570/ TiO_2 -B72, which showed KH570/ TiO_2 -B72 has excellent permeability and can be a good material for bone relics conservation.

CONCLUSIONS

Functional TiO_2 was modified and dispersed successfully in acrylate copolymer through graft copolymerization of acrylate monomers. The structure and properties of the copolymer were characterized by FT-IR, FE-SEM, DSC, TGA, UV-vis, and discoloration. Considering the ultraviolet absorption and transmittance, the optimum dosage of the functional TiO_2 in the copolymer was 0.1 wt % according to the result of UV-vis. The results of FT-IR, FE-SEM, and DSC confirm that the functional TiO_2 were grafted onto the macromolecular chains. After the functional TiO_2 grafted, the acrylate copolymer showed excellent photo-oxidative stability with no effect on the thermal stability via TGA. When the functional TiO_2 added was 0.10 wt %, ultraviolet light aging tests for 648 h showed that the acrylate copolymer film had high ultraviolet absorption, high transparency and excellent photo-oxidative stability with color difference $\Delta E < 1$ in comparison with the blank sample. After ancient ivory was coated with the acrylate copolymer, the appearance and chemical structure of the specimen did not change. This acrylate copolymer could be a potential protective agent for ancient ivory or any other bone relics.

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