Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

THE FIXATION OF NATURAL QI-LACQUER ON SILICATE SURFACES BY ELECTRON-BEAM INDUCED POLYMERIZATION

Ingo Rogner[a]; Heinz Langhals[a]
[a] Institut für Organische Chemie der Universität München, München, Germany

Online publication date: 29 March 1999

To cite this Article Rogner, Ingo and Langhals, Heinz(1999) 'THE FIXATION OF NATURAL QI-LACQUER ON SILICATE SURFACES BY ELECTRON-BEAM INDUCED POLYMERIZATION', Journal of Macromolecular Science, Part A, 36: 3, 461 — 469
To link to this Article: DOI: 10.1081/MA-100101542
URL: http://dx.doi.org/10.1081/MA-100101542

J.M.S.–PURE APPL. CHEM., A36(3), pp. 461–469 (1999)

NOTE

THE FIXATION OF NATURAL QI-LACQUER ON SILICATE SURFACES BY ELECTRON-BEAM INDUCED POLYMERIZATION

Ingo Rogner and Heinz Langhals*
Institut für Organische Chemie
der Universität München
Karlstrasse 23, D-80333
München, Germany

ABSTRACT

A method for the conservation of aged qi-lacquer layers (urushi) on silicate material such as terracotta has been described. The layer of lacquer has been treated with methacrylic monomers and solidified with electron beam radiation. The method is of importance for curators.

INTRODUCTION

The change of polymeric bindings with time is an important factor for the aging of objets d'art. The detachment of qi-lacquer layers (urushi) from the basic material would result in the loss of paint layers and solidifying such layers is a central point in the conservation of such works of art. The terracotta army of the Chinese Emperor, Qin Shihuangdi in Lintong, China is one of the most important archaeological objects and is a prominent example for such problems because the paint layer is bound to the terracotta surface by a qi-lacquer intermediate layer [1]. This layer has changed during the long time of 2200 years buried in wet clay so that it detaches from the surface if air humidity drops below

* Author to whom correspondence should be addressed.

84%. These conditions are present even during excavation of the colored fragments. Until now, the conservation of these paint layers is an unsolved problem.

EXPERIMENTAL

Electron beam curing experiments were carried out at the Institut für Polymerforschung (IPF) in Dresden with the Russian electron accelerator ELV-2, INP Nowosibirsk. A sketch of the electron accelerator is shown in Figure 1. Electron energies can be varied between 0.6 to 1.5 MeV, the maximum radiation current amounts to 25 mA.

The electron beam (EB) is focused and scans the substrate. Extensive shielding is required due to bremsstrahlung. The absorbed dose the sample receives as a result of passing under the beam is obtained by integration of the

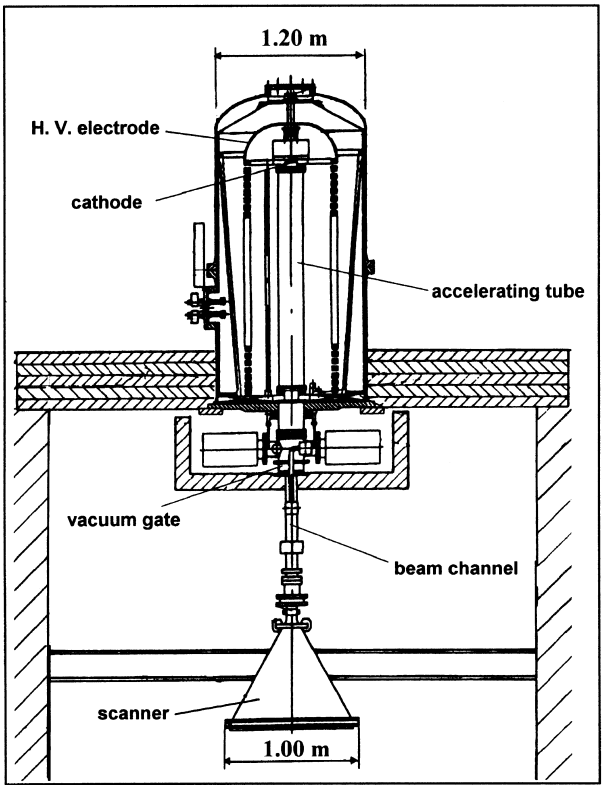

Figure 1. Sectional sketch of the electron accelerator ELV-2, INP Nowosibirsk.

Gausian function for the beam shape. The sample speed is thus inversely proportional to the absorbed dose. In the experiment the dose was administered in steps of 10 and 100 KGy. The total dose absorbed is the sum of all the individual doses.

For all experiments, an electron energy of 1 MeV was used. This value determines how deep the radiation can penetrate into a substrate. At an energy of 1 MeV electrons can penetrate up to 5 mm into a medium of density 1 (water), with a maximum intensity at 1.6 mm. At longer EB exposures if all monomers are consumed by the polymerization reaction main chain scission is possible.

The following monomers were used for EB curing to rebind original qi-lacquer ground layer and aged lacquer (lacquer containing 10% rice starch, aged with H_2O_2/ NH_4OH) onto a terracotta support:

PEG-MA (polyethyleneglycol-methacrylate M_n = 360 g/mol),

PEG-DIMA (polyethyleneglycol-dimethacrylate Mn = 400 g/mol),

TEG-DIMA (triethyleneglycol-dimethacrylate M = 286.3 g/mol),

Plexilith 322 and Plex 6803-1 (both 2-hydroxyethyl-methacrylate (HEMA) based formulations).

Original qi-lacquer ground layer and aged lacquer were flattened on a terracotta support with H2O dest. and were impregnated during three days with the consolidants. The consolidant concentration in aqueous solution was increased stepwise 33%, 66%, 100%. Samples were transported with a cotton wool pad soaked with the undiluted consolidant.

In order to detect deterioration caused by EB curing four different lacquer sample types were subjected to different electron beam doses ranging from 10 to 300 kGy. The four samples were original Qin-dynasty qi-lacquer, artificially aged qi-lacquer, newly prepared samples of a qi-lacquer and a qi-lacquer with the addition of 10% rice starch (additive believed to be used in the Qin-dynasty).

The samples were subjected to the relatively low dose of 10 kGy for a few times. The three polyethylene-methacrylates consolidated at 20-30 kGy, the two HEMA formulations polymerized at an energy dose of 50 to 60 kGy. All consolidants polymerized within the lacquer and the terracotta, however after a few days the samples consolidated with the three polyethylene-methacrylates detached from the terracotta support. Polymerized HEMA shows the best results concerning the mechanical strength of the binding of the qi-lacquer. Unreacted monomers on the surface evaporated after a few days. After several months the

original Qin-dynasty qi-lacquer is still firmly bound to the terracotta, the surface is not shining or lustrous and the terracotta has completely dried.

DTA/TG measurements were performed with a Netzsch STA 409 EP thermoanalysis apparatus in the temperature range of 20 to 600°C. Only monomers of polyethyleneglycol-methacrylate (PEG-MA) and polyethyleneglycol-dimethacrylate (PEG-DIMA) produced solidified polymer films on the terracotta surface after EB curing. The two HEMA formulations therefore could not be investigated by DTA/ TG. The thermoanalytical investigation of PEG-MA found a glass transition temperature of Tg = 65°C and exothermic peaks at 193°C, 333°C and 486°C.

For PEG-DIMA, a glass transition temperature of Tg = 115°C and exothermic peaks at 171°C, 232°C and 336°C were measured. The Tg reflects the crosslink density, therefore, the lower Tg is recorded from the polymerized monofunctional monomer PEG-MA. Qi-lacquer consolidated with PEG-MA or PEG-DIMA unfortunately did not bind properly to the terracotta, therefore, both consolidants will not be used in the future.

In order to polymerize monomers within the lacquer samples with X-rays, experiments were carried out with the Faxitron 805 X-ray source. The accelerating voltage can be varied between 8 to 110 kV with a maximum current of 3 mA. Original qi-lacquer samples were impregnated with PEG-MA, HEMA, HEA and Plex 6803-1, Plexilith (both formulations containing HEMA).

All samples were subjected to 10, 50 and 110 kV for five minutes at a distance of 32 cm from the X-ray source. After this, the samples with HEMA and with Plexilith were again irradiated at 8 kV for ten minutes at a distance of 46 cm from the source. X-rays easily penetrate materials because of the minute interaction with material of low density too few radicals are formed to promote polymer formation.

In all cases, no polymerization was apparent after the experiment.

Samples for IR spectra were obtained by taking off a thin layer of the lacquer surface with a scalpel. The samples were pulverized in an agate ball mill and measured as a KBr pellet with a Perkin-Elmer 1000 IR spectrometer. In order to evaluate a deterioration of qi-lacquer, four different sample types were subjected to different electron beam doses ranging from 10 to 300 kGy. Both original Qin-dynasty qi-lacquer and artificially aged lacquer showed similar spectra before and after irradiation, no specific change could be observed. Newly prepared samples of a qi-lacquer and a qi-lacquer with the addition of 10% rice starch (additive believed to be used in the Qin-dynasty) produced identical spec-

tra before and after irradiation by the electron beam. Infrared spectroscopy identifies no deterioration of the qi-lacquer by EB radiation.

Laser desorption mass spectroscopy (LDMS) was carried out on irradiated samples. The degree of polymerization of the applied monomer and possible EB cure damaging effects were monitored. For laser desorption a XeCl excimer laser LPX-100 Lambda Physik (308 nm, 30 ns pulse width) was used. The positively charged ions generated were separated by a non-commercial reflectron time-of-flight mass-spectrometer (RETOF-MS) with a mass resolution of $m/\Delta m = 2000$ [5]. In contrast to most commercial systems, the laser desorbed ions were allowed to drift for ca. 2 cm before being extracted by a pulsed electric field. The ions were detected by dual multichannel plates and the signal was collected by a digital oscilloscope. The spectra were then transferred to a PC for further evaluation. The delay between laser pulse and ion extraction allows one to preselect the mass of the ions detected.

Laser desorption of newly prepared qi-lacquer and a qi-lacquer with the addition of 10% rice starch was performed for unirradiated samples and samples subjected to electron radiation at 300 kGy. Mass spectra of each sample were taken at three different laser fluences. At all fluences mass spectra of the sample before and after EB radiation were alike. Mass-spectroscopical evaluation shows no damaging effect of the EB radiation on the qi-lacquer.

To prove the polymerization of the applied monomers within the terracotta and the original qi-lacquer LDMS spectra were taken. Preceding investigations with matrix-assisted laser desorption and ionization (MALDI) were carried out using various matrices. Unfortunately, this technique produced mass spectra with matrix fragments disguising the sample spectra.

LDMS of HEMA polymerized by electron beam curing determined the average polymer chain length in the terracotta support and within the qi-lacquer. The spectra are depicted in Figure 2.

Upper spectrum shows HEMA polymerized within the solidified original qi-lacquer layer.

Lower spectrum depicts HEMA polymerized within the terracotta support.

In the terracotta support short polymers mainly consisting of 2-4 monomer units were detected, whereas within the solidified original qi-lacquer layer solely polymers with 4-6 monomer units were found. For every polymer, a combination of peaks can be observed. This is due to sodium and lithium adduct peaks [6] and because of the cleavage or addition of a hydroxyethyl fragment (small bond dissociation value). In the mass spectrum of HEMA polymerized in

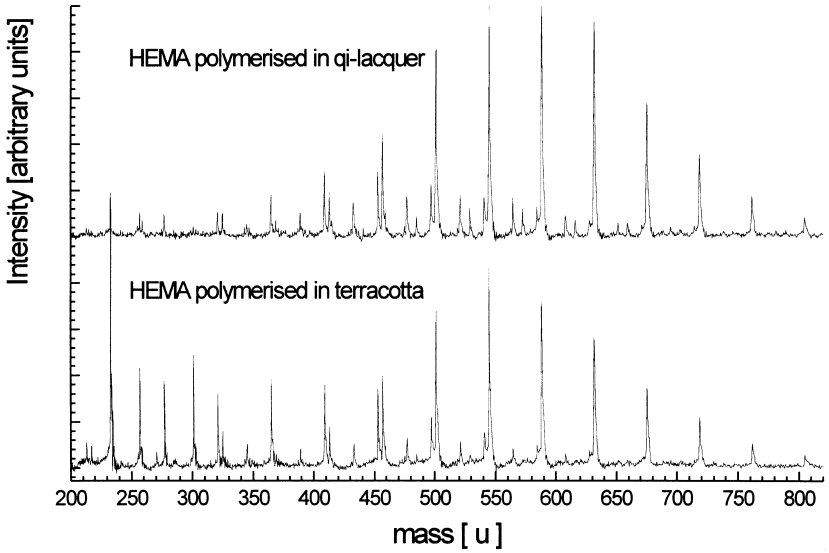

Figure 2. Laser desorption mass spectra of hydroxyethyl-methacrylate (HEMA) polymerized by electron beam curing.

terracotta fewer lithium adduct peaks can be found. Furthermore, hydroxyl end-groups are detected which were formed through EB radiation by reaction with the terracotta.

Further investigations will include light microscopy of a cross-section of qi-lacquer attached to the terracotta. This technique will show the degree of penetration of the monomers and the electron beam into the terracotta.

RESULTS AND DISCUSSION

We tried to rebind the qi-lacquer layer to the terracotta by the application of organic polymers. This seems to be an extraordinarily difficult problem if the support is not an organic material, but a highly hydrophilic surface of a silicate such as terracotta. The application of radical initiators and monomers such as methacrylic esters, solidified the qi-lacquer, but could not bring about a firm connection of the lacquer to the terracotta support. Inorganic pigments constitute the polychromy of the conserved works of art. A second problem was the lustrous surface of the solidified material which impairs the visual impression by changing the tonality of the colors.

We wanted to avoid these problems by the application of a two-step process. Firstly, the terracotta and the overlying layers were impregnated with cotton wool compresses containing the liquid monomer. The monomer concentration in water was increased to 100% in several steps. During this process, unwanted polymerization was inhibited by the stabilizers which are generally added to the monomers to allow storage (up to 650 ppm hydroquinone-monomethylether). Thus, the monomer had enough time to penetrate all organic and inorganic material.

Secondly, the polymerization was induced. This could be done neither by conventional thermal radical initiators nor by photopolymerization, which was prevented by the dark color of the lacquer layer. Therefore, we tried initiation by penetrating radiation by which we could start polymerization from within the terracotta support.

Polymerization by the application of X-rays gave very poor results. The photons were not absorbed properly within the thin qi-lacquer layer and the silicate material to induce polymer formation. Very high radiation doses would cause pigment damage.

However, good results were obtained by the application of an electron beam for initiation which forced the start of polymerization within the terracotta propagating toward the outside through the monomer impregnated qi-lacquer to the air. After the electron radiation is switched off, there is no radioactivity left within the irradiated material; of course there is very intense X-ray radiation during the application of the electron beam which must be thoroughly shielded. Methyacrylic monomers were of special interest as solidifying materials because of their long lifetime and their excellent transparency. Methylmethacrylate seemed to be less suitable because of its low polarity so that water soluble 2-hydroxyethyl-methacrylate (HEMA) gave even better results. It was applied as a commercial formulation Plex 6803-1 (Röhm). Detachment of consolidated qi-lacquer by volume shrinking of HEMA cannot occur because of the thin HEMA layer and because of the short chain length of only 4-6 monomer units.

Polymerized HEMA can take up to 40% mass of water. This implies that the polymerized product lets water penetrate. If applied to wet terracotta, water can cross the polymerized HEMA film and evaporate. In contrast to a film which seals the surface, the formation of blisters can be avoided.

The application of an electron beam (EB) initiates a radical polymerization which is inhibited by molecular oxygen contained in air [2]. Oxygen therefore must usually be thoroughly excluded to obtain a smooth and solid surface.

On the other hand, the influence of oxygen is desirable for obtaining a lusterless surface of solidified works of art. Therefore, one should initiate the polymerization with electron beam radiation with air surrounding the monomer soaked qi-lacquer layer. After the EB cure small residues of monomer can easily be removed from the surface by wiping off or by evaporation of the monomer at room temperature.

A central difficulty in conserving paint layers by the application of electron beam polymerization is the potential damage of the lacquer by radiation. Ions and radicals remaining after the radiation process can be starting points for further decay. The qi-lacquer, however, contains ortho-hydroxy phenyl moieties [3] which are known to be radical scavengers.

We, therefore, have thoroughly investigated the influence of electron radiation on qi-lacquer by IR and mass spectroscopy and have found that even a dose of 300 kGy (30 Mrad) does not result in a detectable damage of the qi-lacquer. However, this dose is far beyond the dose which is necessary for polymerization. Additionally, the radiobiological effect of electron beam and bremsstrahlung destroys micro-organisms and can be used to disinfect contaminated lacquer [4].

The application of the rapid electron beam polymerization is therefore, a promising method for the conservation of the terracotta army of Qin Shihuangdi and other objets d'art. The results of further investigations will be reported elsewhere.

ACKNOWLEDGEMENTS

We thank the BMBL and the Fonds der Chemischen Industrie for financial support, Professor Dr. Oskar Nuyken for helpful discussions, the Institute for Polymer Research in Dresden, Germany, the Museum of the Terracotta Warriors and Horses in Lintong, China (Managing Director, Wu Yongqi, Professor Zhou Tie, Professor Zhang Zhijun, and He Fan), and the Bavarian State Conservation Office.

REFERENCES

[1] C. Herm, C. Thieme, E. Emmerling, Wu Yonqi, Zhou Tie, and Zhang Zhijun, *Analysis of Painting Materials of the Polychrome Terracotta Army of the First Emperor Qin Shihuang*, The Ceramics Cultural Heritage, 1995, pp. 675-684.

[2] R. Mehnert, *Radiation Chemistry*, Ullmanns Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A22, 1993, p. 481.

[3] Ju Kumanotani, *Urushi (oriental lacquer) - A Natural Aesthetic Durable and Future-Promising Coating*, Progress in Organic Coatings, 1995, 26, pp.163-195.

[4] ARC-Nucléart: La désinfection, http://www-dta.CEA.fr/wwwcea/nucleart/fr/desinfec.htm, (July 22, 1998).

[5] I. Rogner, P. Birkett, and E. E. B. Campbell, *Hydrogenated and Chlorinated Fullerenes Detected by "Cooled" Modified Matrix-Assisted Laser Desorption and Ionization Mass Spectroscopy (MALDI-MS),* Mass Spectrometry and Ion Processes, 1996, 156, pp. 103-108.

[6] C. G. de Koster, Marc C. Duursma, Gerard van Rooij, Ron M. A. Heeren, and Jaap J. Boon, *Endgroup Analysis of Polyethylene Glycol Polymers by Matrix-Assisted Laser Desorption/Ionization Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry*, Rapid Communications in Mass Spectrometry, 1995, 9, pp. 957-962.

Received October 19, 1998