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Original article

# Epoxy polymer Hxtal NYL-1™ used in restoration and conservation: Irradiation with short and long wavelengths and study of photo-oxidation by FT–IR spectroscopy

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ABSTRACT

Hxtal NYL-1™ is an epoxy adhesive designed especially for glass restoration and conservation, which however is used today on marble, wood, ivory and much more; it can also be colored or filled to match porcelain. This epoxy system is claimed by the manufacturers to have excellent photostability. The present study aimed at the estimation of its photostability under irradiation with light of $\lambda = 254$ nm or $\lambda > 300$ nm in the presence of oxygen (air) for a certain period of time towards samples cured at different temperatures. The changes of chemical structure caused by the irradiation of samples were studied by FT–IR spectroscopy. The general conclusion of this study is that the best temperature for curing of Hxtal NYL-1™ is that of 25 °C and that irradiation even with light $\lambda > 300$ nm must be avoided because may cause photo-oxidative reactions.



## 1. Introduction

Hxtal NYL-1™ is an epoxy adhesive developed by Herbert V. Hillary with the assistance of the Texaco and Shell laboratories in 1983 and was available from Conservation Materials Ltd [1]. Unlike other epoxies that were made for hobbyist, home and industrial uses, Hxtal NYL-1™ was designed especially for restoration and conservation and not borrowed from another field. The primary use of Hxtal NYL-1™ is glass and china mending [2]. However, it can be also used on porcelain, marble, wood, ivory and much more; it can be colored or filled to match various types of porcelain [3,4]. The reactive epoxides are usually prepared by condensation of epichlorohydrin most often with bisphenol A, their reaction product is commonly known as the diglicidyl ether of bisphenol A (DGEBA) (monomer or oligomer, usually mixture of these). Hxtal NYL-1™ is prepared by reaction of a cycloaliphatic epoxy resin with a mixture of amines used as curing agents that is the epoxy resin is a hydrogenated analog to the DGEBA. The absence of aromatic rings makes the resin UV resistant and suitable for outdoor applications, while also reduces its viscosity. In our previous works, the cure kinetics of Hxtal NYL-1™ was investigated at different isothermal reaction temperatures (25, 50, 75 or 100 °C) using Fourier transform–infrared spectroscopy (FT–IR) [5,6] and differential scanning calorimetry (DSC) [6]. These techniques permit the follow of curing process over time and thus the determination of the optimum time for the maximum curing and the maximum degree of curing (DC%) obtained at each studied temperature.

In outdoor situations, polymers are subject to UV light deterioration. Generally, the photodegradation of epoxy resins may be classified into two categories: short wavelength degradation and long wavelength degradation. The former occurs around 254 nm wavelength, whereas the long wavelength degradation occurs with UV light at 295 nm and above and is more representative of actual solar radiation. The short-wave photolysis is mainly characterized by absorption of UV light, followed by photophysical and/or photochemical processes and coloration reactions. Epoxy polymers are generally very sensitive to UV light and obviously their photodegradation mechanism depends on their chemical structure. Photodegradation leads to discoloration and to a deterioration of its physical properties [7]. The term yellowing is frequently used to describe this phenomenon. However, some polymers yield brownish and sometimes even different colors; so the term discoloration is more preferred than yellowing. This discoloration is frequent with epoxy adhesives currently used for glass and non-porous ceramics restoration. In the case of glass, this phenomenon is particularly unsightly and understanding its origins could contribute to prevent steps to avoid its occurrence [8]. Hxtal NYL-1™ is claimed by its manufacturers to be the only epoxy adhesive known that does not yellow upon exposure to light. It owes its stability to its

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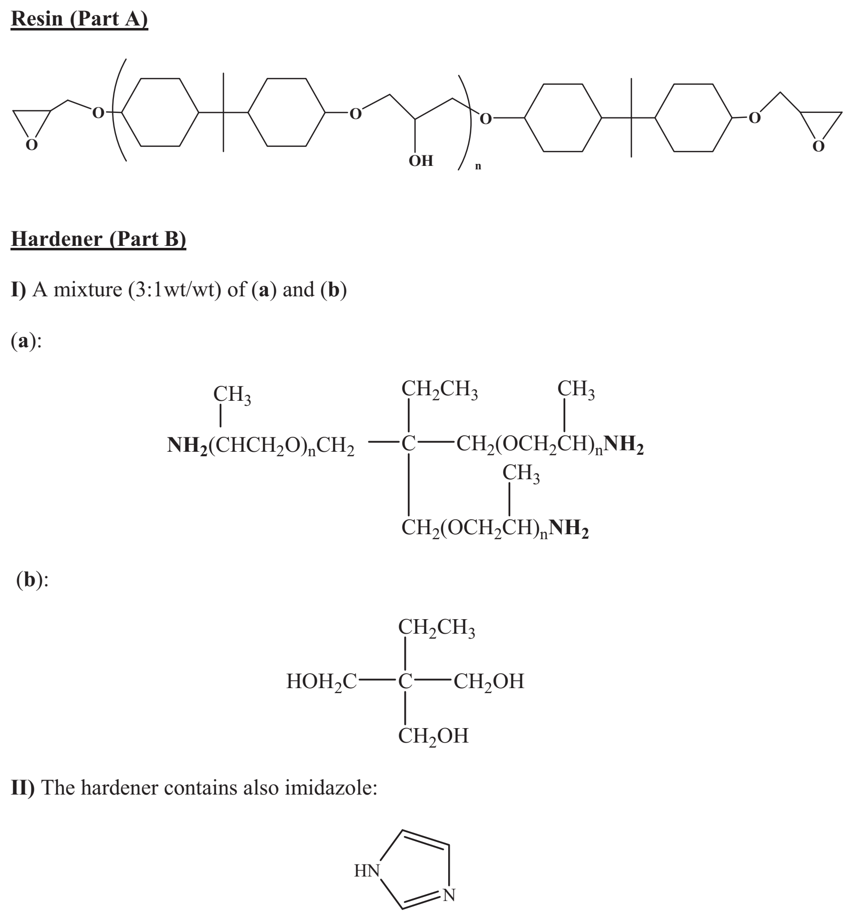


**Scheme 1.** Chemical structure of resin (part A) and hardener (part B) of Hxtal NYL-1™.

ultra-purity; the traces of metal ions removed during the manufacture and purification of Hxtal NYL-1™ are responsible for the development of color in ordinary epoxy adhesive [1]. However, it is also reported that the high stability of Hxtal NYL-1™ against UV light is due to the absence of an aromatic ring in its structure [9]. The resistance of Hxtal NYL-1™ to yellowing under high-intensity light aging was studied for the first time many years ago, in 1986, by Jane Down [10]. Films of Hxtal NYL-1™ were prepared and the absorption at 380 and 600 nm was measured on a UV-spectrophotometer. Then, the films were aged in a Weather-Ometer equipped with a 6500-W xenon arc lamp and infrared absorbing filters (at 22 °C and 50% humidity, the ideal museum conditions). The films were removed from the aging chamber at specific time intervals and the absorption at $\lambda = 380$ and $\lambda = 600$ nm was measured. The degree of yellowing ($A_t$) of films observed at a specific time were then calculated from the equation: $A_t = [A(380\,nm)_t - A(600\,nm)_t] \times 0.1/F$ where $F$ is the average film thickness [10,11].

In this work, samples of Hxtal NYL-1™ were cured at 25, 50, 75 or 100 ± 1 °C for 9 days, 3 days, 23 h or 6 h correspondingly; these curing times were found in our previous work to be the optimum for each curing temperature used [5,6]. The samples were then irradiated with light either 254 nm for 7 days maximum or with light above 300 nm for 3 weeks maximum. The changes in the chemical structure of the samples caused by irradiation were followed by FT–IR spectroscopy. The environmental conditions for glass art exposure in museums usually include 20 ± 2 °C temperature, 50 ± 10% relative humidity, 30 nm the lowest illumination and display windows of high-silica and low-alkali glasses, without restriction in exhibition times. It was considered interesting and useful for conservation experts to accelerate the epoxy degradation in harsh, destructive wavelength so to see the future long-term effect of the light on the adhesive, along with the smoother exposure of UV–Vis.

## 2. Experimental

### 2.1. Raw materials

Hxtal NYL-1™ was supplied by Restorer Supplies Inc, Golden, Colorado and it consists of two parts the part A (epoxy resin) and the part B (hardener); the chemical structure of their ingredients according to the manufacturer is shown in Scheme 1. More data for the two components are reported in reference [5]. Both components are stored in dark-colored glass containers at 4 °C, in absence of light [12,13].

### 2.2. Samples preparation

Hxtal NYL-1™ is prepared by mixing 3 weight parts of resin to 1 weight part of hardener according to the suggestion of the manufacturer. The weighting was performed with a Mettler Toledo AG285 balance with accuracy ± 0.0001 g into a plastic container, made by a high-density polyethylene. Part A and B were homogenously mixed by stirring at room temperature for 60 s and subsequently were degassed.

Polyester films of 0.1 mm thick with a rectangular space hole of 3 × 5 cm were placed between two slides of glass (5 mm thick) covered with polypropylene sheets. Then, a drop of the glue was transferred in the middle of the hole and “sandwiched”, taking care not to entrap air bubbles while the glass plates were joined