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A methodological approach for monitoring the curing process of fairing compounds based on epoxy resins

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ABSTRACT

Epoxy resins, heavily loaded with fillers, are used as fairing compounds in coating systems to fill superficial imperfections and protect the hull of yachts and ships; they are complex composite materials whose final performance can be heavily affected by the conditions of application. In this paper the curing process of an innovative formulation was studied in function of the temperature and humidity, in order to evaluate how these environmental parameters influence the reaction evolution and gain further insight into the reaction mechanism.

The study of the curing process was carried out by thermogravimetric analysis, differential calorimetric analysis and FT-IR spectroscopy.

From the thermal analysis the obtained crosslink degree ranged between 92 and 99%, at 10 °C and 25 °C respectively. The samples cured at 25 °C reached the maximum curing degree in one week independently from the humidity. The samples cured at lower temperature (10 °C), even after two weeks, did not reach the complete crosslinking. On the other side, it was evident that the humidity did not influence the curing at 25 °C, while it had a slight effect at lower temperature (10 °C).

Results from FTIR spectroscopy at 25 °C evidenced changes in the bands characterizing the two components of the resin during the curing reaction, in particular the disappearance of the oxirane ring band.

1. Introduction

Within the production of the naval sector a very important role is played by coating systems for vessel external surfaces, which are most exposed to aggressive environments, such as seawater or marine atmosphere, and thermal variations. According to the SOLAS regulation (Safety of Life and Sea), the coating systems protecting the hull must guarantee a minimum duration of 15 years with minimal maintenance. Therefore it is evident the necessity of accurately formulating these materials in order to obtain long lasting performances. The coating system are typically composed of: primer (~100 μm), fairing compound (~2 cm), finishing fairing compound (~300 μm), tie coat (~100 μm), undercoat (~100 μm) and topcoat (~50 μm).

Fairing compounds and putties are composite materials whose application is crucial for smoothing the surface, filling possible defects or voids and contributing to isolate the hulls. In particular the high thickness of fairing compounds is a critical aspect from the mechanical point of view. As a consequence, more and more often these composites are considered in the design of the boat and a lot of numerical simulations are performed at design stage. Then, it is of primary importance for the designer to know the parameters that influence the curing process. Unfortunately very few studies are available in literature for these specific materials [1–3].

The formulation includes one-component or two-component resins, fillers and additives. The two-component resins consist of an epoxy resin (A component) and a curing agent or hardener, mainly based on amine group (B component); once mixed in appropriate ratios, they crosslink, forming infusible, insoluble and rigid products [4,5]. The type and concentration of the hardener, the temperature and the humidity of the environment of application affect the curing process of epoxy resins. Moreover the degree of cure has a high impact on the physical, mechanical and chemical properties of epoxy systems [6,7].

Since the curing process of an epoxy thermoset is thermally-activated and temperature dependent, the thermal analysis is the most common method to monitor this process. In general, thermal analysis is the study of the state or change of state of a material in terms of temperature [8–15].

Indeed, the differential scanning calorimetry (DSC) has been widely used as a method to determine cure kinetics of thermoset resins, with the analysis of glass transition temperature (T_g) and enthalpy of

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reaction (ΔH_r) variation.

On the other hand, infrared spectroscopy (Near-Infrared and Mid-Infrared) turned out to be well suited for analyzing the degree of cure for epoxy systems and the reaction at molecular level, directly by analyzing structural changes [16–20]. The FTIR spectroscopy offers several advantages: at first, it allows to monitor the curing process over the whole conversion range. Although during the curing the material undergoes several state transitions, these transitions have limited influence on the vibrational spectrum. Secondly, by selecting the appropriate signals, it is possible to monitor simultaneously all the concentration profiles of the various reacting species present in the system, which is the only way to obtain direct mechanistic information [21].

On the basis of these techniques, the main aim of the work is to evaluate the crosslinking degree of samples cured in different environmental conditions, i.e. temperature and humidity, and understand their effect on the reaction evolution and completion.

2. Materials and methods

The standard material used in this study is an high-build epoxy two-component ultra-light filler, whose composition is the following:

Component A - modified epoxy resin from bisphenol A and bisphenol F, benzyl alcohol, hollow glass microspheres, thixotropic agent;

Component B - mixture of polyamide resins with an epoxy-polyamide adduct, inert filler, benzyl alcohol, hollow glass microspheres, thixotropic agent;

The mixing ratio of Component A and Component B was 2:1 (w/w).

The approximate composition after mixing the two components is reported in Table 1.

The reported data, for each experiment, are the average of three single measurements carried out on the same sample.

A Mettler-Toledo thermal gravimetric analyzer (TGA/DSC 1 Star^e System) is used to determine the degradation temperature of the resins. A heating rate of 10 °C/min is used operating in the range 30–700 °C in nitrogen atmosphere (gas flow of 80 ml/min), and in the range 700–900 °C in oxygen atmosphere (gas flow of 80 ml/min).

The glass transition temperatures (Tg) and the enthalpies of reaction (ΔH_r) of the resins, and their variation during the curing process, are evaluated using a Mettler-Toledo differential scanning calorimeter (Model DSC 1 STAR^e System).

Resins (component A + component B) are left in an oven at the temperature of 80 °C for different lapses (2.5, 5, 7.5, 15, 20, 30, 40, 60, 240 min). Once the samples reached the predetermined residence time in the oven, a quenching in liquid nitrogen took place and DSC measurements followed. By this procedure it is possible to obtain characteristic curves of each sample at the different curing times. The DSC profile for this analysis is set from −100 °C to 280 °C, at heating rate of 20 °C/min.

In addition, in order to evaluate the crosslinking degree of the samples cured in different, temperature and humidity conditions, four experiments are carried out:

i) samples cured at 25 °C and absolute humidity 1 g/Kg or relative humidity (RH) 7%, (dry environment) for 24, 48, 72, 96 and 168 h.
ii) samples cured at 25 °C and absolute humidity 6 g/Kg or RH 30% for 24, 48, 72, 96 and 168 h.
iii) samples cured at 10 °C and absolute humidity 1 g/Kg or RH 7% (dry environment) for 24, 48, 72, 96, 168 and 336 h.
iv) samples cured at 10 °C and absolute humidity 6 g/Kg or RH 80% for 24, 48, 72, 96, 168 and 336 h.

Table 1
Composition of the fairing compound.

Components	% w/w
Resin (A + B)	60–70
Inert filler	20–30
Glass microspheres	10–20
Benzyl alcohol	0–2
Thixotropic additives	2–4

The parameter combinations are chosen based on the realistic application conditions: room temperature and low temperature in dry and wet atmosphere. For these evaluations the DSC profile is set from −10 °C to 280 °C, at heating rate of 20 °C/min.

IR spectra are collected by means of a FT ThermoFisher Spectrometer (OMNIC acquisition software, DTGS detector, for each spectrum 100 scans were averaged). Different acquisition procedures are used. Reference spectra of component A and B are obtained in Transmission method by spreading the pure components on a self-supporting KBr disk (IR-grade KBr, from Aldrich). The curing of the two components at 25 °C is followed directly on a KBr support recording spectra every 4 s for 12 h consecutively (OMNIC Series software, for each spectrum 4 scans were averaged) in order to evaluate changes in functional groups during the curing process. The final reticulated product in the form of powder has also been analyzed after grinding and mixing with KBr powder and pressed in a self-supporting disk.

The UV–vis and Near IR spectra are recorded by a JASCO Instrument equipped with a Diffuse Reflectance accessory (JASCO acquisition software).

Several NIR and UV–vis analyses are performed on samples with different A:B ratios, 1:1, 1.3:1, 2:1, 2.7:1, 3.3:1.

3. Results and discussion

TGA analysis is performed to determine the degradation temperature of the resins.

As it clearly emerges in Fig. 1, the sample shows a first loss at around 150 °C, due to the loss of low molecular weight molecules contained into the fairing compounds. Then the loss of material in the range 300–700 °C is due to real decomposition of the organic part of the resins, confirming their thermal resistance up to 350 °C. Moreover, at 700 °C, it is observed the switch from N_2 to O_2 atmosphere and the residue resulted 38% wt, ascribed to the inorganic filler.

The DSC plots of the heating profile of the resins after different times of curing are reported in Fig. 2.

The evaluated ΔH for each sample resulted very reproducible, with an error lower than 2%.

By increasing the treatment time in the oven, the value of the enthalpies of reaction decreases and the glass transition temperatures increase due to the increase of crosslinking in the thermosetting resins.

The curing degree (CD%) is evaluated through the variations in the

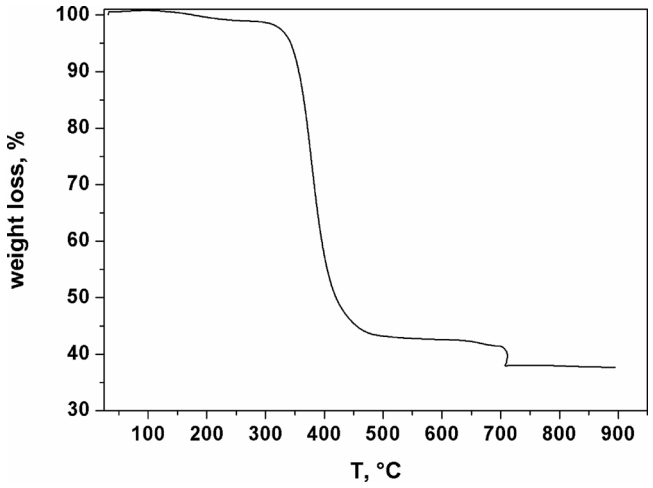

Fig. 1. TGA measurement of epoxy resins.