

Technical Note

Mounting of lead/acid battery positive-plate materials in epoxy matrices: an investigation of instances of excessive heating

A. F. Hollenkamp

CSIRO Division of Mineral Products, P.O. Box 124, Port Melbourne, Vic. 3207 (Australia)

(Received July 10, 1992)

Abstract

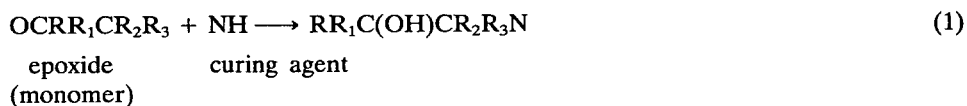
Epoxy resins are often employed as the media for mounting lead/acid battery samples, as preparation for microscopic examination. Occasionally, it is found that large quantities of heat, well in excess of those expected for normal epoxy curing reactions, are liberated during the mounting of sections of positive-plate material (mainly lead dioxide). This leads to the destruction of samples and creates a hazardous environment. In an initial study of the problem, the ambient temperature and the residual acid content of the plate material have been selected as the factors most likely to contribute to excessive heating. An investigation has shown that neither factor exerts a direct influence over the course of epoxy curing reactions. It appears, therefore, that instances of thermal runaway are determined by a complexity of parameters and laboratory procedures should take into account the possibility of such heating phenomena.

Background

One of the tasks carried out routinely in lead/acid battery research is the impregnation of positive plates (or portions thereof) with thermosetting epoxy resins. The main reason for this procedure is to provide physical support so that the plate materials may be cut for the viewing of cross sections. Experience in these laboratories has shown, however, that a large amount of heat can be liberated from the sample, after the introduction of the resin. On occasion, the quantity of heat has been sufficient to melt the lead or lead alloy grid present in the sample, yet in no case has there been an obvious reason for the apparent thermal runaway. Clearly, this situation represents a potential safety hazard. The most immediate danger of the 'hot' sample initiating a fire has been countered by basic house-keeping measures. Even if fires are avoided, the reactions observed to date have generated copious volumes of noxious fumes that pose a health hazard to those in the vicinity. In addition, a potentially important positive-plate sample is lost on each occasion. For these reasons, a detailed study of the factors that may influence the course of epoxy-setting reactions, and hence the heat evolved, has been conducted. The results are reported here for the benefit of other groups engaged in research that utilizes epoxy-mounting of battery-plate samples.

Introduction

In order to assess the factors that may contribute to sample heating, it is necessary to consider the reactions that constitute the curing of epoxy resins. An epoxy resin is commonly defined as a molecule that contains one or more epoxide groups. An epoxide group is a residue of oxirane, a three-membered heterocyclic compound with the formula, C_2H_4O . Although the term epoxide refers strictly only to the heterocyclic moiety of the epoxy compound, it is more often used to describe the whole compound. Similarly, reference to a particular epoxy resin is usually made with a typical commercial blend of epoxy compounds in mind, rather than a single species. The curing of an epoxy resin is based on the nucleophilic attack, by a specified curing agent, of the alpha or beta carbon atom of the epoxide group, as shown for the general case in reaction (1);



The desired properties of curing agent are satisfied by a wide range of compounds, such as amines, alcohols and thiols. Therefore, a so-called 'epoxy system' is a two-part preparation, the components of which are mixed in a ratio that is given by the manufacturer's specifications. Importantly, reaction (1) is exothermic so that some degree of sample heating will always occur. The main point of this investigation was to determine whether the presence of lead/acid battery materials causes an increase in the amount of heat evolved from the curing of epoxy resins, thereby compromising the usefulness of the resins. This possibility has been explored by monitoring the temperature of vacuum-impregnated battery plates during thermosetting of the resin.

Curing reactions of epoxy resins are thought to proceed via ionic intermediates that are formed by initial nucleophilic attack at one of the epoxide carbon atoms. The presence of acidic species is known to increase the rate of curing by the enhancement of the initial opening of the epoxide ring [1]. This effect is significant in the mounting of lead/acid battery materials because of the presence of sulfuric acid. Even when battery plates are washed with large volumes of water, the high porosity and small average pore size prevent the complete removal of acid. Drying of the washed plate at $\sim 100^\circ\text{C}$ results in concentration of the residual acid because mainly water is lost. Thus, the resulting sample may contain an appreciable quantity of sulfuric acid; one that is, perhaps, sufficient to accelerate the curing reaction. This possibility was investigated by controlling the amount of residual acid in several plate samples and monitoring the heat evolved during subsequent curing. Another potential source of protons for acceleration of curing reactions is the positive active material. It is known that significant quantities of hydrogen can be adsorbed onto the large surface area of these materials during service.

Finally, it is possible that the large quantities of heat arise, not from an enhancement of curing, but from other reactions between the battery material and one, or both, of the mounting agents. Lead/acid positive plates consist mainly of a porous mass of lead dioxide attached to a grid (current collector) of lead or lead alloy. The former is a strong oxidant and may well be capable of oxidizing some of the compounds present. For example, the hardener employed in this study is based on the compound isophorone diamine and the amine groups are oxidizable under moderate conditions. Alternatively, the alkene group of isophorone diamine may be oxidized, via a well-known reaction, by residual sulfuric acid. The behaviour of the resultant sulfate

derivative(s) in the curing process is a point for speculation. It is certain, however, that appreciable quantities of these derivatives are likely to alter both the rate of curing and the properties of the product.

Experimental details

The experiments involved monitoring the temperature of several batches of epoxy resin after impregnation of washed and dried positive plates. The latter were all of approximately the same weight and physical dimensions. Each had been subjected to at least 20 charge/discharge cycles after which, the porous material consisted almost entirely of lead dioxide. Of the ten plates considered in this study, six were washed with distilled water, until the washings were substantially free of acid (<0.005 M). With the remaining four plates, two plates were washed with a 0.005 M solution of sodium hydroxide until the pH of the washings had risen to that of the base solution (pH=9) and two plates were not subjected to a washing step. All plates were dried at 105 °C for 16 h. Plate treatment is summarized in Table 1.

Plates were placed in shallow trays fashioned from either tin or aluminium. The epoxy used was obtained from Ciba-Geigy Australia Ltd., and consisted of Araldite LC 274 resin and Araldite LC 249 hardener. Each plate was mounted in 160 cm³ of the resin-hardener mixture. The latter was introduced under vacuum. Temperature was monitored by an electronic transducer. Several experiments were also conducted in which the effect of ambient temperature on the course of epoxy curing was assessed. The curing of 40 cm³ batches of resin, with and without positive-plate material present, was examined at temperatures of between 29 and 35 °C.

Results and discussion

Unfortunately, this section represents something of an anti-climax as not one of the impregnations conducted in the laboratory produced any sign of excessive heating. Water-washed plates exhibited temperature rise of only 3 to 8 °C. No signs of sample damage (e.g., darkening of resin) were observed. A typical profile of sample temperature with curing time is shown in Fig. 1. Plots for the alkaline and acidic plates were similar and increases in temperature fell within the range quoted for water-washed plates. Clearly, the final pH of the solution present in the plate prior to drying does not exert any direct effect on the amount of heat output from curing.

The other variable that was considered in this study was the ambient temperature during setting of the resin. This topic was suggested by the observation that many (but not all) of the violent reactions occurred either on days when the temperature

TABLE 1
Treatment scheme for positive plates

Plate type	Treatment
Water-washed	washed with distilled water
Alkaline	washed with 0.005 M NaOH (aq)
Acidic	unwashed

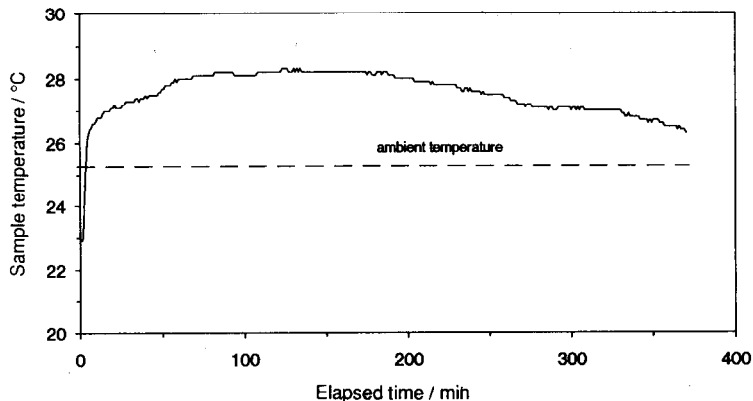


Fig. 1. Plot of sample temperature vs. time for the epoxy mounting of a cycled positive plate.

of the laboratory had risen well above normal ambient levels (20 to 23 °C), or when the sample had been exposed to elevated temperatures in order to speed the latter stages of curing. A series of epoxy preparations was cured at ambient temperatures of up to 35 °C. Some were carried out in the presence of dried positive plate material, while others were simply 'control' curings; no battery material was present. In no case, however, was any acceleration of curing apparent, nor were any side reactions indicated. Thus, ambient temperature does not exert any direct effect on the course of reactions in the battery-material/epoxy system.

Concluding remarks

This study has aimed to gain more information on the conditions that are associated with the liberation of large quantities of heat during the curing of epoxy-impregnated lead/acid positive-plate material. While these violent reactions have largely been isolated incidents, they have posed a serious risk to health and safety in the laboratory on each occasion. This investigation has considered the effects of the two main variables associated with the mounting of battery materials: acidity of the solution left in the plate prior to drying and the ambient temperature of the mounting procedure. The results indicate that neither factor exerts any direct influence on the heat liberated in the curing of the epoxy resin used in these laboratories. The detailed negative evidence assembled here shows that the violent reactions observed are probably the result of a host of factors, additional to the two evaluated. Some of these other factors may be related to subtle variations in the phase composition of the positive plate from which the sample was taken. Systematic study of such variables will always be problematic.

Further indications of the complex nature of the situation are suggested by the following observations:

- (i) excessive heating has been noted both early in the curing process (i.e., when the resin is still free flowing) and many hours after the resin has become solid;
- (ii) usage of nonaqueous solvents, in a final washing step before drying, does not remove the problem; for example, a recent heating incident occurred with a section of plate that had been washed with acetone prior to drying.

In summary, it can be stated that there is no aspect of the current procedures employed in these laboratories for the mounting of lead/acid positive plates that can be linked directly to the violent reactions that have been observed. Nevertheless, it is the author's opinion that raising the temperature of the epoxy-hardener mixture to any level above normal room temperature should be avoided. This applies especially to the placement of cured or partly cured (gelled) samples in ovens for extended periods. While no link between ambient temperature and the unwanted reactions has been established, it is likely that the latter will be favoured by higher temperatures, simply on kinetic grounds. Allen [2] has even suggested that mounting of battery materials should be carried out under thermostated (room temperature) conditions in which all excess heat is conducted away from the sample. The samples produced in the present study were found to be suitable for cutting and polishing, without being held at elevated temperature after the resin had solidified. Placing the impregnated sample in an oven at 40 to 50 °C, after the resin has gelled, serves only to increase the speed of curing which is, of course, slower in the semisolid state. Complete curing will, however, eventually take place at normal room temperature (20 to 25 °C) if sufficient time is allowed. The latter procedure is therefore recommended whenever possible. In order to minimize further the exposure of workers to the hazards described here, correspondence on similar instances and remedies is welcomed.

Acknowledgement

The author is grateful to Mr D. Bieniak (Ciba-Geigy Australia Ltd.) for helpful discussions on various aspects of this study.

References

- 1 *Epoxy Resins: Chemistry and Technology*, in C. A. May (ed.), Marcel Dekker, New York, 1988, p. 401.
- 2 M. D. Allen, *Microstruct. Sci.*, 6 (1978) 31.