Journal of Thermal Analysis, Vol. 31 (1986) 1091–1100

CURE BEHAVIOR OF AN EPOXY-PHENOLIC MAGNETIC RECORDING INK*

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(Received September 12, 1985; in revised form January 13, 1986)

The curing behavior of an epoxy-phenolic coating containing a thermoplastic additive and iron oxide is described. Cure response was measured on a DuPont 981 Dynamic Mechanical Analyzer (DMA) and a Perkin–Elmer TGS–2 Thermogravimetric Analyzer (TGA). Samples coated onto a glass fiber ribbon were cured isothermally in the DMA, allowed to cool, and then scanned to measure the glass transition and related phenomena. During cure the thermoplastic additive was observed to phase separate, as evidenced by a secondary damping peak near its glass transition temperature. Above 200° oxidative reactions made a major contribution to the cross-link density. Isothermal TG in air and nitrogen showed evidence for oxygen uptake and an oxidative weight loss at temperatures $>200°$. Iron oxide, oxygen content of the purge gas, and flow rate of the purge gas were observed to affect cure behavior.

A typical coating used for magnetic recording is described. In the simplest of terms this coating may be viewed as a mixture of thermosetting resins, a thermoplastic additive, solvents, and iron oxide. The curing of thermosets and their study by thermal analysis have been reviewed by this author [1]. As the name suggests, thermosetting resins become set, i.e. intractable and insoluble, as a consequence of the chemical cross-linking reactions accompanying cure. As with most formulations, this magnetic recording ink requires heat for curing. The resulting coating, if properly formulated and processed, is a highly cross-linked, three-dimensional infinite network with good magnetic properties and good durability.

The curing of thermosets is complex in that several steps are involved. The cure begins by formation and linear growth of polymer chains, which soon begin to branch, and then to cross-link. As the reaction proceeds, the molecular weight increases rapidly and eventually several chains become linked together into networks of infinite molecular weight. This sudden and irreversible transformation

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* Presented at 13th NATAS Conference, Philadelphia, PA, September 1984.

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from a viscous liquid to an elastic gel, which marks the first appearance of the infinite network, is called the gel point.

Gelation is characteristic of thermosets, and it is of foremost significance. From a processing standpoint, gelation is critical since the polymer does not flow or heal and is no longer processable beyond this point. Beyond the gel point reaction proceeds toward the formation of one infinite network possessing the dimensions of the entire sample and with substantial increases in cross-link density, glass transition temperature, and ultimate physical properties.

Another phenomenon, distinct from gelation, is vitrification of the growing chains or network. Vitrification is dependent on both degree of conversion and cure temperature, and may occur at any stage of the cure. This transformation from a viscous liquid or elastic gel to a glass begins to occur as the glass transition temperature of these growing chains or network becomes coincidental with the cure temperature. Further curing in the glassy state is extremely slow and, for all practical purposes, vitrification brings a halt to the cure process. Vitrification is a reversible transition, and if cure is incomplete it may be resumed by heating to devitrify the partially cured thermoset. The onset of vitrification causes a shift from chemical control to diffusion control of the reaction, and it may be observed by a gradual decay of the reaction rate.

The literature often describes the curing of thermosets which might be called "ideal systems" [1–4]. Such systems possess well-defined characteristic parameters such as T_{c0}, the temperature below which the completely unreacted thermoset is in the glassy state and therefore unreactive; $T_{c,gel}$, the cure temperature at which gelation and vitrification occur simultaneously; and $T_{c\infty}$, the minimum cure temperature required to achieve "complete cure". Corresponding characteristic glass transition temperatures are T_{g0}, $T_{g,gel}$ and $T_{g\infty}$. One of the more common discrepancies between these and real thermosetting systems is the inability to define a unique state of complete cure or 100% conversion which is independent of reasonable changes in temperature or other variables. It is more common to define an optimum cure which may include the specification of temperature, environment, etc., in which case ideal behavior serves as a valuable reference or starting point. The magnetic coating described here is a good example of a non-ideal thermosetting system, but one which can benefit from a thermoanalytical investigation of its cure.

Experimental

Coating

The subject of this study is a typical magnetic coating ink. It consists of a DGEBPA-type epoxy phenolic resole cross-linkable binder, a thermoplastic additive, iron oxide magnetic particles, and solvents. All samples were coated onto 11–12 mm wide glass DMA ribbons supplied by DuPont. Ribbons were coated by dipping them in the ink and removing excess ink with a glass stirring rod. Samples were allowed to dry for approximately three days in a hood and then exposed to lab ambient prior to analysis. Coated thickness of almost dry, uncured ribbons was $\simeq 0.15$ mm = 6 mils.

Dynamic Mechanical Analysis (DMA)

All analyses were performed on a DuPont 981 Dynamic Mechanical Analyzer in the horizontal mode. The DMA was programmed with a DuPont 1090 Thermal Analyzer. The glass fabric samples were cut to $\simeq 17$ mm lengths before being mounted in the DMA. The driven and passive arms of the DMA were separated by 11.0 mm.

All samples were cured in the DMA at isothermal temperatures between 105 and 260°, with cure times ranging from 1 to 6 hours. Samples were cured in air, nitrogen (<10 ppm oxygen), or a carefully controlled blend of the two. Except where noted the flow rate was maintained constant at 8 liters/min. The effect of flow rate on cure was studied by varying it from 0.7 to 20 liters/min. The DMA cure consists of a constant heat-up to temperature at the maximum achieveable rate of $\simeq 22$ deg/m, followed by the desired time at temperature. Subsequent to curing all samples were allowed to cool in the DMA in nitrogen. Most were immediately scanned at 5 deg/min in nitrogen from 40 to 370° to measure the glass transition; in addition some samples were cooled to $-160°$ to measure low temperature transitions in addition to the glass transition. The glass transition temperature, T_g, is taken as the onset of the frequency break. Three damping phenomena were observed: an α-transition associated with the glass transition and occurring at 10–15° higher temperature than T_g, a β-transition which is attributed to the thermoplastic additive, and a γ-transition which is a low temperature transition in the epoxy-phenolic matrix. The α-peak temperature has the advantage of being more reproducible and easier to measure than T_g.

Thermogravimetric Analysis (TG)

Dynamic and isothermal TG were measured on samples from an uncured DMA ribbon. Measurements were performed on a Perkin–Elmer TGS–2 Thermogravimetric Analyzer which was programmed with a System 4 microprocessor controller. A paper punch was used to prepare sample specimens of 5.0mm diameter. Isothermal experiments were run in both air and nitrogen; all dynamic experiments were performed in air at a heating rate of 20 deg/m. Flow rates of both gases were 45 cm^3/m. Isothermal curing schedules were as close as possible to those for DMA, i.e. samples were heated to temperature at 22 deg/m and held for the required times.

Results and discussion

Cross-linking and transitions

A comparison of air curing with nitrogen curing is shown in Figure 1a, demonstrating that the majority of cross-links in this coating are oxidative in nature. Because of the composite nature of the samples and the complex stress fields in the horizontal mode of the DMA, it is impossible to quantify the ratio of oxidative to chemical cross-links; however, it is estimated to be much greater than one. The determination of gel times is indicated as the extrapolated onset of frequency increase, which is equivalent to the back-extrapolation to zero modulus.

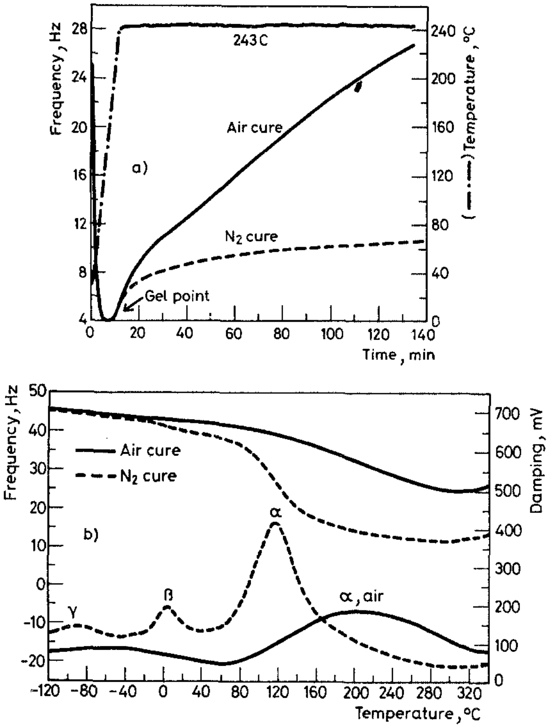

Fig. 1 a) Isothermal curing of the magnetic coating ink in air and nitrogen. b) Frequency and damping subsequent to cure; 5 deg/min in nitrogen. DuPont 981 DMA

Gel times for air and nitrogen curing are identical, occurring during the heat-up portion at $\simeq 10$ minutes into the cure cycle.

The large differences in dynamic mechanical properties between coatings cured in air and nitrogen are illustrated in Fig. 1b. The nitrogen cured coating has three distinct transitions: an α-transition $\simeq$ 120°, a β-transition near 0°, and a γ-transition at $\simeq -90°$. Other experimentation has shown that the α-transition is due to the glass transition of the epoxy-phenolic reaction product, and the β-transition to the glass transition of the thermoplastic additive. The γ-transition is felt to be attributable to the cross-links formed in the epoxy-phenolic. In contrast, the air cured coating has only two transitions. The α-transition has shifted up to the 200° region and become very broad, and there is a small secondary transition at $\simeq -40°$. Indicative of its higher cross-link density, the air cured coating shows a much smaller decrease in modulus at T_g ($\propto$ frequency^2) and a reduced level of damping.

The appearance of a separate damping peak and broadening of the main peak (Fig. 2) suggests that phase separation occurs at an early stage of the cure, resulting in an epoxy-phenolic rich phase and an additive rich phase. When cured in air, the additive rich phase forms early in the cure process but later disappears as a result of oxidative processes. Oxidative cross-linking can be seen to result in very broad, shallow damping behavior, possibly due to the variety of cross-links formed.

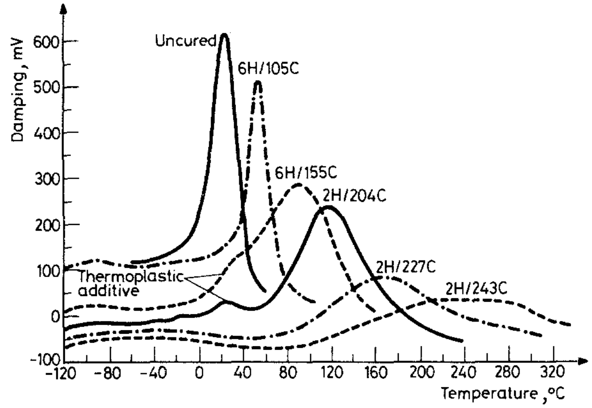

Fig. 2 Damping behavior of magnetic coating at different stages of air cure

The effect of iron oxide on air curing is illustrated in Fig. 3. Two effects of the oxide can be seen: a small decrease in the gel time, and a major increase in cross-link density. The decrease in gel time is attributed to the acidic iron oxide surface which catalyzes the chemical cross-linking reactions. The very high cross-link density, which requires the presence of both air and iron oxide, demonstrates that the oxide

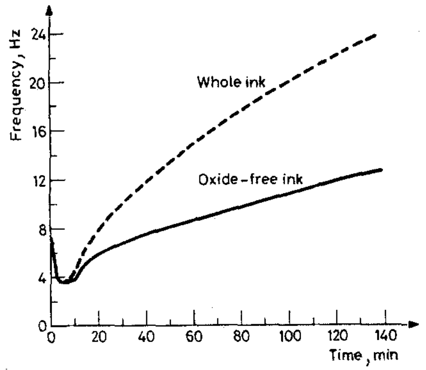

Fig. 3 Effect of iron oxide on air cure. α-peak temperatures: whole ink ≃210°; oxide-free ink ≃130°

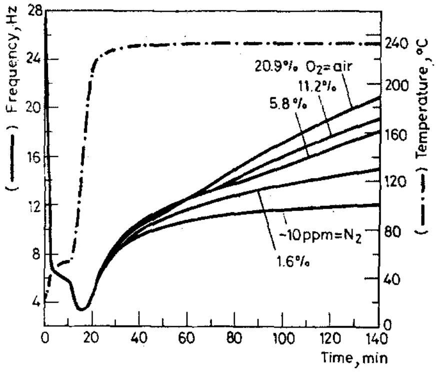

Fig. 4 Effect of oxygen content of purge gas on cure

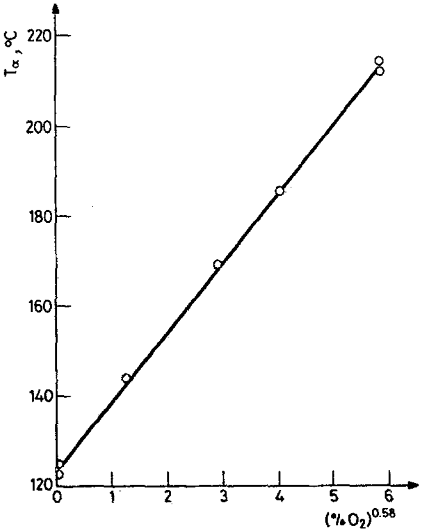

Fig. 5 Approximate square root dependence of oxygen on cure

plays an active role in the oxidative cross-linking process. Comparison of the nitrogen cures of whole coating with oxide-free coating also shows evidence for reinforcement by the oxide. The effect of oxygen content during cure of the whole coating ink is shown in Fig. 4. Measurement of the glass transition subsequent to these cures revealed an approximate dependence on the square-root of the oxygen content (Fig. 5). The flow rate during air cure was observed to have a large effect; very little effect of nitrogen flow rate was seen (Fig. 6).

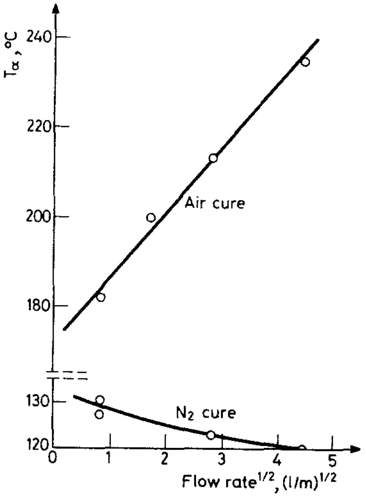

Fig. 6 Effect of purge gas flow rate on cure

Weight losses associated with curing and degradation

Thermogravimetric curves of uncured coating ink on a DMA ribbon is shown in Fig. 7. The weight scale has been normalized to the approximate weight of ink. Weight loss is seen to begin immediately on heating with the loss of retained solvents, which are estimated to be ≃2% for this sample. The broad weight loss which reaches a maximum rate at ≃220° also accompanies the cross-linking reaction between epoxy and phenolic, and is attributed to the combined loss of condensation products (water and formaldehyde) and volatile components of the phenolic resin. Four decomposition reactions are identified: a doublet, A and B, peaking at ≃345 and ≃360°, respectively; reaction C at ≃420°; and reaction D at ≃470°.

Weight losses during air and nitrogen cure are shown in Fig. 8. Weight loss in nitrogen totals 10%, with 9% occurring in the first 30 minutes. Comparison of the dynamic TG of the nitrogen cured coating with uncured coating ink suggested that the weight loss during cure consisted predominantly of the solvent, condensation

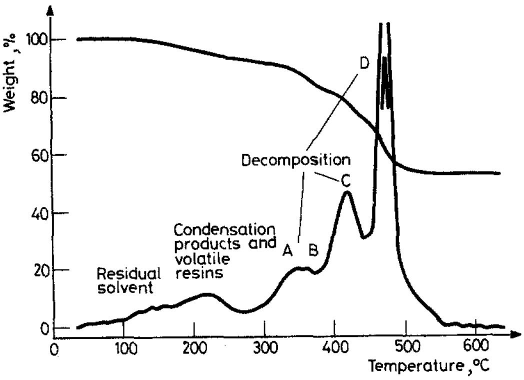

Fig. 7 Thermogravimetric analysis of uncured magnetic coating ink. 6.0 mg, 20 deg/min in air. Perkin–Elmer TGS–2

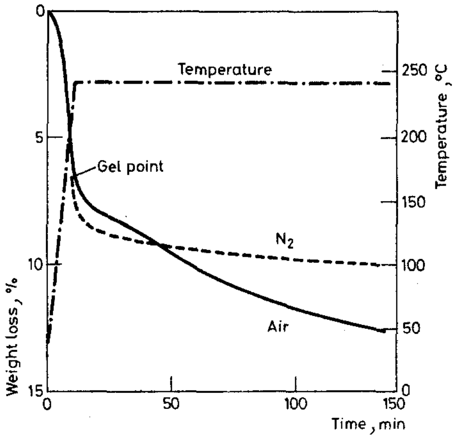

Fig. 8 Weight loss during cure of magnetic coating ink. Gel time from DMA (Fig. 1a)

cross-linking products, and volatile resins. The weight loss process in air is more complex. The first 6–7% is identical to that for the nitrogen cured sample. The lesser weight loss in air between 10 and 40 minutes is interpreted as oxygen uptake in the first part of the oxidation process. Figure 1a suggests that oxidative cross-linking commences with the apparent oxygen uptake. At 30–40 minutes there is an increase in the weight loss rate (Fig. 8, air) and in the cross-linking rate (Fig. 1a, air). The dynamic TG of this sample showed the absence of reaction peak C, diminishment of peak B, and lowering of the temperature of peak D. The absence of iron oxide was observed to diminish the oxidative weight loss.

Time-temperature effects

The development of cross-link density with time at five isothermal temperatures is shown in Fig. 9. Several important aspects of the curing process are evident. A plateau in the cross-link density is reached only at the highest temperatures and/or longest times. Coatings cured to the plateau possess very little damping, tend to be brittle, and may be severely resin deficient due to binder weight loss. After 4 hours at 260° a decrease in the frequency is seen, indicating a degradation in the modulus or cross-link density. From the shape of the higher temperature traces an additional reaction is observed to begin at about 14 Hz, where the rate of cross-link formation increases. A commensurate increase in weight loss rate is also observed (see, for example, Fig. 8, air). From a time-temperature superposition analysis [5] the activation energy for this reaction is estimated to be about 23 kcal/mol.

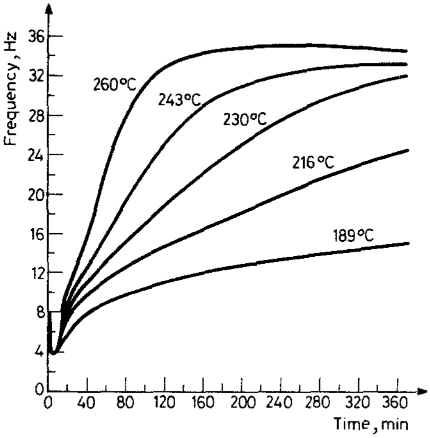

Fig. 9 Isothermal DMA in air at several cure temperatures

Conclusion

The curing behavior of an epoxy-phenolic coating containing a thermoplastic additive and iron oxide is very complex, and probably best described in terms of its deviation from ideal behavior. During cure the thermoplastic additive phase separates, as evidenced by a secondary damping peak near its T_g. This behavior is similar to that observed for rubber-modified epoxies [6]. Above 200° oxidative reactions promoted by iron oxide make a major contribution to the cross-link density. Characteristic parameters for this coating are $T_{g\infty,N2} \simeq 95°$ and $T_{g\infty,air} \simeq 270°$, the glass transition temperatures (onset of frequency break) for coating cured to completion in nitrogen and air, respectively. Isothermal TG in air and nitrogen showed evidence for oxygen uptake and an oxidative weight loss. The curing of this coating thus involves phase separation of the thermoplastic additive, chemical and oxidative cross-linking, and chemical and oxidative weight loss. Iron oxide, oxygen content of the purge gas, and flow rate of the purge gas were observed to affect cure behavior.

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Zusammenfassung — Das Aushärtungsverhalten von ein thermoplastisches Additiv enthaltenden epoxy-phenolischen Überzügen wird beschrieben. Die Aushärtung wurde mit einem DuPont 981 Dynamic Mechanical Analyzer (DMA) und einem Perkin–Elmer–TGS–2 Thermogravimetric Analyzer (TGA) gemessen. Auf Glasband aufgebrachte Proben wurden isotherm im DMA ausgehärtet und nach dem Abkühlen aufgeheizt, um die Glastransformation und damit zusammenhängende Phenomäne zu messen. Während des Aufheizens wurde eine Phasentrennung unter Ausscheidung des thermoplastischen Additivs beobachtet, was durch einen sekundären Dämpfungspeak nahe der Glastransformationstemperatur angezeigt wird. Oberhalb 200° tragen oxydative Reaktionen im größeren Umfang zur Vernetzungsdichte bei. Die isotherme TG in Luft und Stickstoff liefert Beweise für eine Sauerstoffaufnahme und einen oxydativen Gewichtsverlust bei Temperaturen über 200°. Eisenoxid sowie Sauerstoffgehalt und Strömungsgeschwindigkeit des Spülgases beeinflussen das Aushärtungsverhalten.

Резюме — Исследовано отверждение эпоксифенольных покрытий, содержащих термопластические добавки и окись железа. Характеристики отверждения были измерены на Дюпон 981 динамическом механическом анализаторе (ДМА) и на Перкин–Эльмер ТГС–2 термогравиметрическом анализаторе (ТГА). Образцы, нанесенные на ленты из стекловолокна, изотермически отверждались а ДМА, затем охлаждались и после этого измерялись их температуры стеклообразования и родственные эффекты. Во время отверждения термопластических добавок наблюдалось фазовое разделение, подтверждающееся наличием вторичного пика затухания около температуры стеклования. Выше 200° окислительные реакции вносят главный вклад в образование поперечных связей. Изотермический метод ТГ, проведенный в атмосфере воздуха и азота, представил доказательство потребления кислорода и окислительной потери веса при температурах выше 200°. Установлено, что наличие окиси железа, содержание кислорода в продувном газе и скорость его потока, оказывают влияние на процесс отверждения.