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A study of the curing process of paint on metal utilizing thermal stimulated current (TSC) and relaxation map analysis (RMA) [1]

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Abstract

The purpose of this work is to illustrate the use of the process of thermally stimulated current (TSC) for the analysis and control of crosslinking and curing of paints on metal substrates. The study of the crosslink density and/or cure ratio for paint on metal is vital, not only in the final quality inspection of a finished part, but also in the development of new resins and processes for paints and coatings.

INTRODUCTION

Thermally stimulated current (TSC) and relaxation map analysis (RMA) are analytical techniques based on the study of the response of materials in a direct current field as the temperature changes.

Thermally stimulated current (TSC) refers to the process of heating a sample to a temperature near a transition to be studied, applying a d.c. field to the sample to orient the dipolar groups present, then quickly cooling the sample to a temperature well below the temperature of polarization T_p, to trap the dipoles in the oriented state. While re-heating at a controlled rate, the sensitive electrometer reads the current generated by the dipoles' movement as they return to the original, non-polarized state. The resulting data is then plotted as current versus temperature.

Relaxation map analysis (RMA) is a refined version of TSC in which instead of quenching the sample from the polarization temperature T_p to a very low temperature, the sample temperature is lowered only a few degrees with the polarization field still applied. The polarization field is then removed for a certain time, and the sample is cooled to a low

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temperature. The sample is reheated and the current read as for a TSC experiment. This process, called "thermal-windowing", allows for only a fragment of the total dipoles (those influenced by the polarization field in this temperature region) to be oriented. By scanning around the temperature of the detected transition, while keeping the thermal-window-width constant, the global peak detected by DSC can be broken down into elementary relaxation processes [1]. By deconvolution of the global transition into its elementary processes, it becomes possible to evolve information and data on such important values as the activation energies (ΔH, ΔS, and ΔG), free volume, degree of disorder (DOD), and dielectric constants (ε'', and $\varepsilon' - \varepsilon^{\infty}$).

EXPERIMENTAL

The material studied was a polyester-based paint coating, with crosslinking by a melamine resin, catalyzed with a sulphonic acid. The 0.001″ (25 micron) coating was applied with a wire-wound draw-down bar, over cold-rolled steel that has been pre-treated with iron phosphate and primed with a urethane primer. These samples were processed by the supplier for three conditions: under-cured, correctly cured and over-cured, by varying the bake time. Each sample was cut into small squares approximately 0.25 inches square. The instrument used for the study was the Model 41000 TSC/RMA spectrometer (SOLOMAT TA Instrumentation, Stamford, CT) utilizing both liquid nitrogen and water sample cooling (water for the TSC scans and liquid nitrogen for the RMA scans).

The TSC experiments were carried out using the three samples and the following conditions: first the sample was heated to 120°C, the temperature of polarization T_p, and polarized with 100 V for 2 min. The temperature of the sample was then lowered to 25°C with the polarization field still applied. Upon reaching 25°C, the field was removed and the temperature was allowed to remain isothermal for 2 min. The isothermal stage allows the dipoles oriented by the field, but below the temperature region of interest to their original state. The sample was then heated to 200°C at a rate of 7°C min^{-1}. During the ramp in temperature, the electrometer records the current generated by the relaxation processes of the oriented dipoles. The results of the scans are illustrated in Fig. 1.

A fresh sample was placed in the instrument and the temperature range for the peak detected by TSC was subjected to thermal-windowing experimental using the following parameters: range of study 20–40°C; window width, 2°C; polarization voltage, 50 V; polarization and depolarization time, 2 min.

Each of the convoluted relaxation processes isolated by the thermal windowing technique can be transformed from a current–temperature output to a relaxation line, normally plotted in the Arrhenius plane of

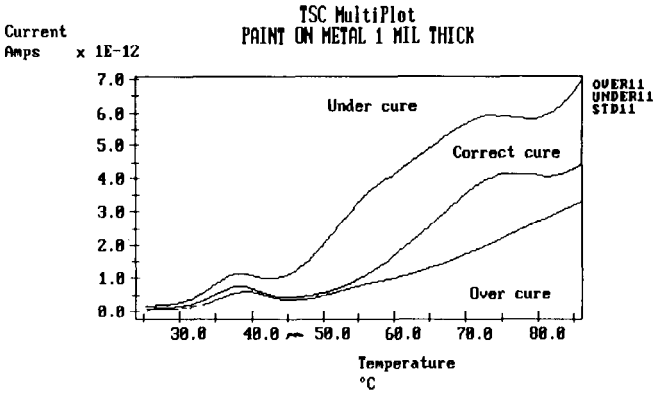

Fig. 1.

coordinates ($\ln \tau$, $1000/T$). The conversion is called an Arrhenius transform of the current data and is fully described elsewhere [2]. The values for the activation energies are automatically determined from the Arrhenius lines curve-fit with linear regression.

RESULTS AND DISCUSSION

The peak observed near 35°C corresponds to the expected glass transition T_g for the polyester component in the paint. The influence of the degree of cure on the peak at 35°C will be the focus of this study.

It has previously been determined that, as a material is subjected to a longer cure time, or higher cure temperature, the peak generated by TSC appears at higher temperatures with a lower intensity as curing increases [3]. This is clearly observed in the study presented here. Figure 2 is a detail of the lower region of Fig. 1, illustrating the temperature and intensity shift as influenced by differing cure times.

Although the test is simple and quick, TSC alone provides substantial information about the relative cure or crosslink density in each sample. In

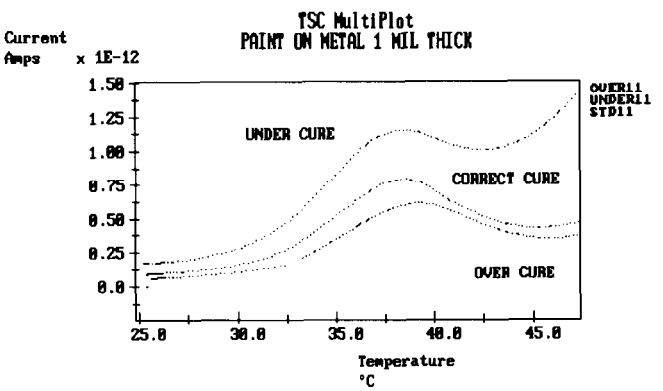

Fig. 2.

this fashion, the technique has been used for incoming quality assurance and process control in many different fields and industries for a number of years.

The plots in Figs. 3–5 illustrate how thermal windowing experiments may be used to deconvolute the global peak that was evident in the TSC scans

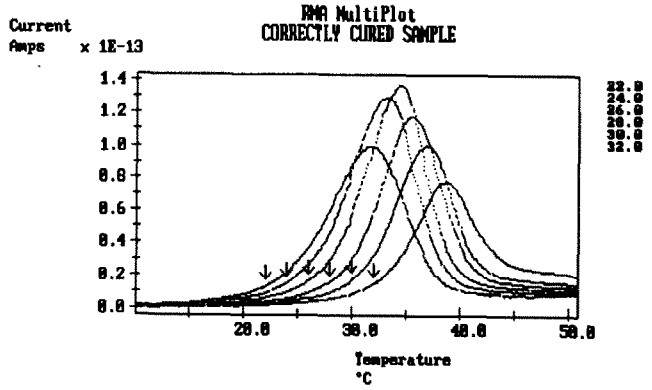

Fig. 3.

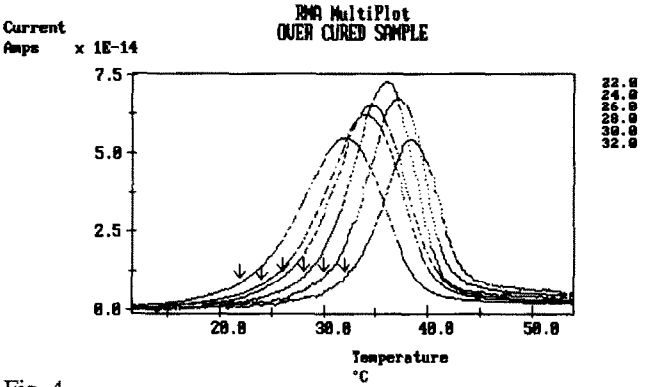

Fig. 4.

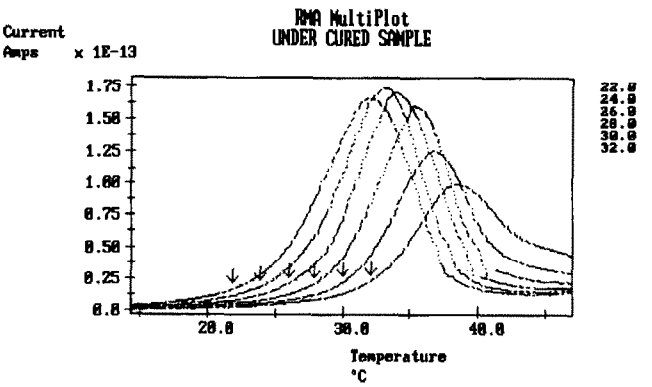

Fig. 5.

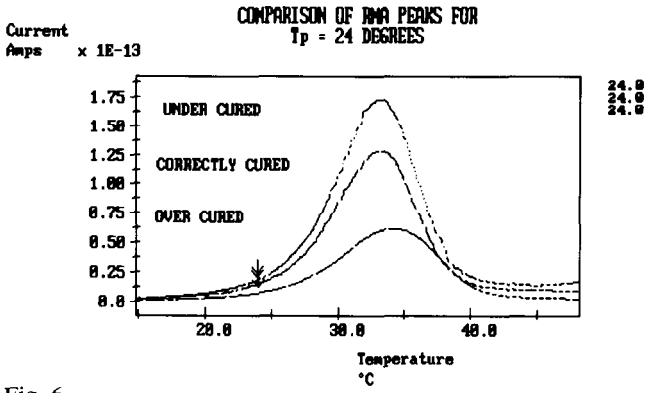

Fig. 6.

(Fig. 1) into elementary, cooperative, relaxation modes. It is important to note that the temperature at peak maximum in the TSC scan often does not correspond to the temperature at peak maximum in the thermal windowing experiments. This is due to the end of one relaxation mode influencing the beginning of another.

Examination of the response for the comparable window-polarization experiment for all three samples ($T_p = 24°C$), reveals the same general phenomenon apparent in the TSC scan (Fig. 6). The peak intensity goes down with cure and the temperature of peak maximum rises slightly.

From the Arrhenius relaxation lines for each of the three curves, it is apparent that the activation energy for the relaxation of the over-cured sample is substantially greater than for the same process in the other two samples. This may be noted by the shift of the intercept of the relaxation line towards higher temperatures and the change in the slope of the line itself (Fig. 7).

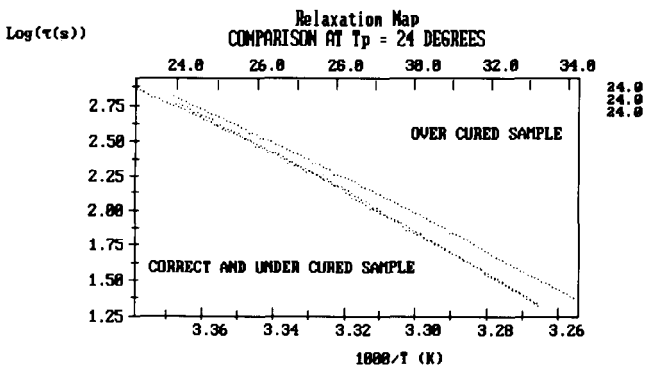

Fig. 7.

DETERMINATION OF THE DOD

A further indication of the extent of the cure is reflected by the degree of disorder (DOD) of each sample resulting from the compensation research [2]. The Arrhenius representation of the relaxation data permits the calculation of the elementary enthalpy of activation, and the pre-exponential factor for the isolated relaxation mode. According to Eyring, the pre-exponential factor in the Arrhenius equation is proportional to the entropy of activation for the activated states involved. When the Arrhenius representations of the RMA scans are all plotted together, the resulting multiple plot is the relaxation map (Fig. 8).

When several Arrhenius lines converge to a single point, this point is called the "compensation point". The coordinates of the compensation point are related to the fundamental properties of the state of the glass (Fig. 9). The significance of the compensation point is that it transcribes the

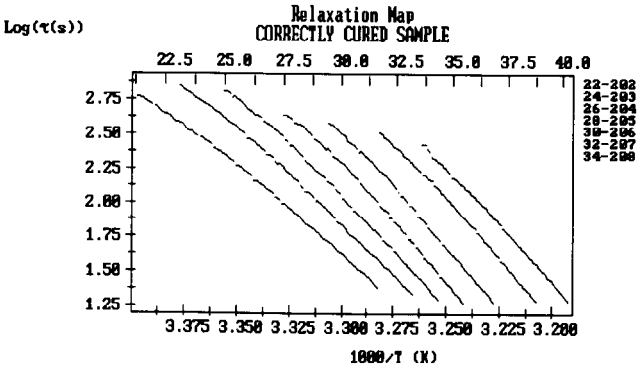

Fig. 8.

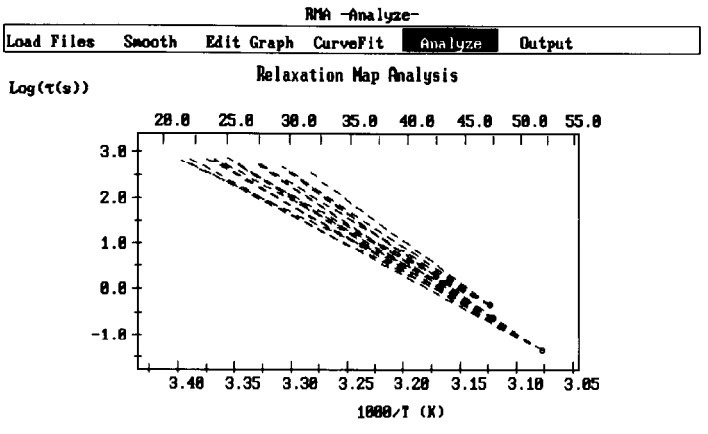

Fig. 9.

coupling characteristics between the different modes of relaxation observed as individual activated processes in the set of converging Arrhenius lines [5]. A very simple and practical way to ascertain whether or not a set of lines converge is to plot intercept versus slope for these lines and assess the linearity of these points. This type of analysis is called a "compensation search". The coordinates of the compensation point are calculated from the slope and intercept of the "compensation line"; the converging point is called the "compensation point".

If a structure is "loose" or less ordered, i.e. when molecular mobility is less hindered by the interactive intra-intermolecular surrounding, the derived entropy of activation will be great. If some influence acts to create order or restriction within the structure, the entropy of activation will be smaller. Therefore, in accordance with Eyring, the activation entropy gives an indication of the degree of disorder (DOD) of the structure. The DOD number is defined from a compensation search as the entropy of activation when the enthalpy ΔH equals zero. This allows comparison between sample structures.

From comparison of the compensation points of each sample (sample 1 refer to the over-cured sample, sample 2 is the correctly cured sample and sample 3 the under-cured sample), and their corresponding DOD numbers, it is apparent that the less cured sample has the highest DOD number. This follows logically as there is less restriction or order in the under-cured system than in the correctly or over-cured systems (Table 1). Once the material approaches and exceeds correct cure, the differences in the compensation temperature, relaxation time and DOD number become less substantial. (As the crosslink density approaches a maximum value, the rate of crosslinking would diminish due to the increase in structure and decrease in the concentration of active crosslink sites within the material.)

The values for the activation energies (ΔS, ΔH, and ΔG), calculated from the relaxation lines are stored to tables using the Solomat software. Other characteristic features of the thermally-windowed depolarization curves, such as frequency equivalent at the maximum, intensity at the maximum, peak area (proportional to the number of dipoles), and relaxation (dielectric) strength ($\varepsilon_s - \varepsilon^\infty$) can also be provided in tabular form for further analysis. An important plot is entropy versus the T_p to determine the temperature of the peak entropy for each sample. This is

TABLE 1

Compensation store

1 Comp = (47.20°C, −0.32 Log(s));	DOD# = 42.44
2 Comp = (47.52°C, −0.61 Log(c));	DOD# = 43.76
3 Comp = (51.94°C. −1.35 Log(s)):	DOD# = 47.11

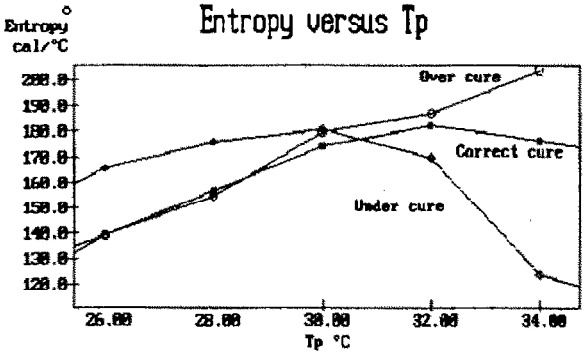

Fig. 10.

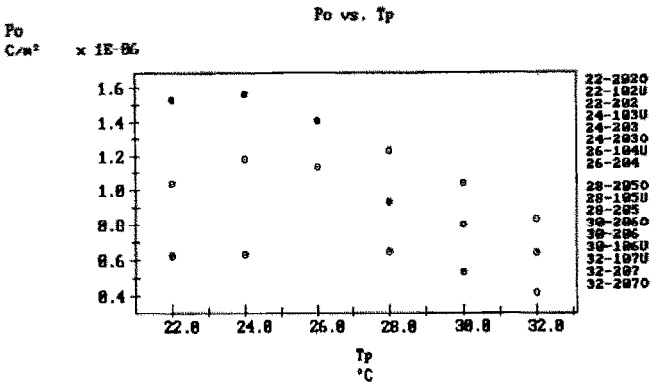

Fig. 11.

very useful in determining not only the glass transition temperature T_g, but also the effect on the material of any processing (Fig. 10).

Another very useful parameter to characterize the degree of cure or crosslink density is P_0, the area under the curve that provides the value of the initial polarization in the sample P_0 (normalized for surface area and heating rate). If the sample has a greater degree of cure (more crosslinking present), there will be fewer dipoles excited by application of the field, and therefore P_0 will be smaller (Fig. 11).

CONCLUSIONS

Thermal stimulated current (TSC) and relaxation map analysis (RMA) have been applied to the curing process of resins and coatings on metallic substrates. A practical application of the technique and available instrumentation have been described for use as a comparative tool for quality and uniformity studies in the paint and coating industry. It has been demonstrated that the values for the compensation temperature, DOD number and other thermokinetic parameters correspond well with variations in product performance.

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