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DYNAMIC MECHANICAL ANALYSIS OF AUTOMOTIVE COATINGS ON A METAL SUBSTRATE *

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ABSTRACT

Dynamic mechanical analysis has been used to characterize the curing of coatings and the cured state T_g of a coating on a standard steel substrate. The glass transition temperature of multi-layer coatings on the substrate were also determined by dynamic mechanical analysis without removing the coatings from the substrate.

INTRODUCTION

Dynamic mechanical thermal analysis, commonly known as DMA, measures the modulus and damping behavior of a sample under an oscillatory force as a function of temperature. This technique has been used extensively for the measurement of the curing profile of thermosetting resins and also the glass transition temperature of thermoplastics and thermosetting resins [1]. However, for the automotive coatings, there are two major challenges, as given below.

(1) Measuring the curing profile of automotive coatings on the standard steel substrate.

(2) Determining the glass transition temperature of multiple layers without removing the paint from the steel substrate.

Figure 1 shows the four layers (E-coat, primer, basecoat and clearcoat) of an automotive paint. E-coat is used for corrosion protection and is electrodeposited onto both sides of the steel. The DMA signal for E-coat is very strong because it is deposited on both sides of the steel. The primer coating is used for specific applications, such as improvement in adhesion strength or impact strength. The basecoat contains colored pigments. The glass transition temperature for the basecoat occurs around or below room temperature. Since the basecoat thickness is of the order of 15 μm, the DMA

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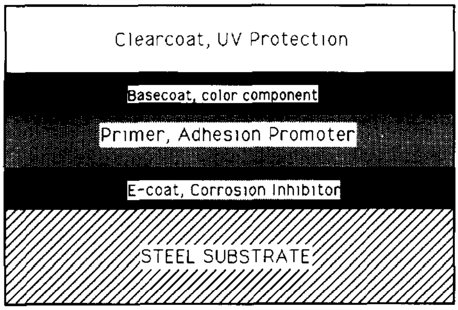

Fig. 1. Different paint layers in an automotive paint.

signal due to the basecoat is very weak in a multilayer sample. The clearcoat is transparent and provides protection against the UV light.

Glass fiber ribbons have been used as a support when measuring the cure behavior of coatings [2] by DMA. The glass ribbon support, however, has several shortcomings. These include, for example, inconsistency of the ribbon itself, difficulty in coating thin uniform coatings and in accounting for electrochemical changes during electrodeposition of coatings. Prime and Adibi [3] measured the T_g of cured magnetic coatings on metal shims using DMA. They concluded that for their magnetic coatings, stainless steel shims of thickness 75 μm gave the optimum results. However, we are interested in measuring the curing profile of coatings on the same type and thickness of steel as used in automobiles.

In the present paper we report the curing profile of E-coat paint on the standard steel substrate used in the automobile industry. The glass transition temperature of the E-coat was measured using both DMA and DSC. The T_g value using DMA was also measured at different frequencies ranging from 0.05 Hz to 10 Hz. It was also possible to determine simultaneously the T_g values of the E-coat, basecoat and clearcoat layers of the automotive paints on the standard steel substrate. The signal from the basecoat is very weak, and it is not possible to determine the T_g value for the basecoat in all multi-layer systems.

EXPERIMENTAL

DMA analysis was carried out on a Du Pont 983 DMA interfaced to a 9900 data station. All measurements were carried out in the vertical mode at 1 Hz except for one E-coat system, where the analyses were run at multiple frequencies ranging from 0.05 Hz to 10 Hz. The horizontal peak to peak displacement was varied from 0.2 to 1.0 mm depending on the sample. The sample preparation is very critical for DMA analysis of coatings on the

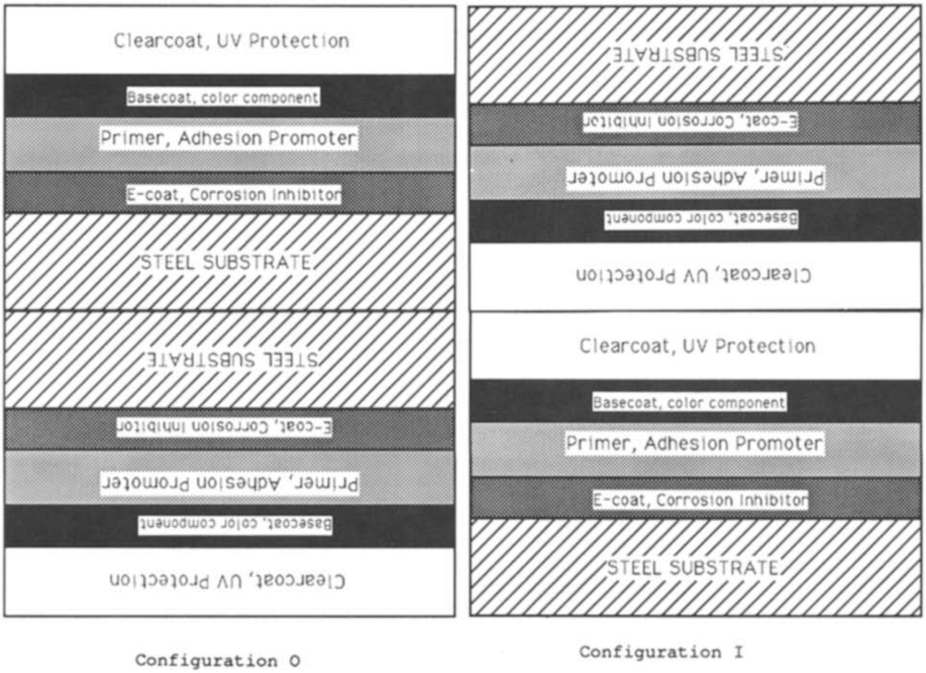

Fig. 2. A two-sample sandwich in two possible configurations.

metal substrate. The sample dimensions were approximately 30 × 10 × 0.9 mm^3 and the sample edges were smoothed with fine sandpaper.

The typical thicknesses for different paint layers were as follows:

E-coat 30–40 μm

Primer 15–25 μm

Basecoat 15–20 μm

Clearcoat 35–45 μm

For the curing profile, the sample was heated from room temperature to 177°C at 25°C min^{-1} and kept isothermally for 60 min at the final temperature. The coating was then allowed to cool to room temperature, and the Tg value was determined either by increasing the temperature in 2°C steps or by scanning at 4°C min^{-1}. The sample was held during three equilibrium cycles at each temperature. For one E-coat the T_g data were also collected at 0.05, 0.1, 0.5, 1.0, 5.0, and 10 Hz and whilst increasing the temperature in 2°C steps.

The multi-layer coatings were also measured as a two sample sandwich, and the two possible configurations are shown in Fig. 2. In one case the clearcoat layers of the two bars face each other; this is called "facing inwards" or configuration I. For the other configuration the clearcoat layers face away from each other; this is called "facing outwards" or configuration 0.

The glass transition temperature of cured E-coat film was also determined by DSC. The E-coat films were scraped off the panel and the DSC sample size was 10–15 mg. The heating rate was 4 °C min^{-1} and nitrogen was passed through at 20 cm^3 min^{-1}. The samples were first heated from room temperature to 180 °C and then cooled. The samples were then rerun from room temperature to 180 °C. The T_g value was determined either as the peak position of the first derivative of the heat flow or as the midpoint in the transition region of the heat flow curve.

RESULTS AND DISCUSSION

The results are divided into two sections. The first section deals with the curing analysis and T_g values of E-coat paints on the steel substrate. The T_g analysis of multi-layer coatings on steel as well as on aluminium substrates are discussed in the second section.

DMA analysis of E-coat on standard steel panel

Figure 3 shows the DMA curing curve for an E-coat paint on a steel panel of thickness 0.8 mm. The modulus of the paint initially decreases owing to a

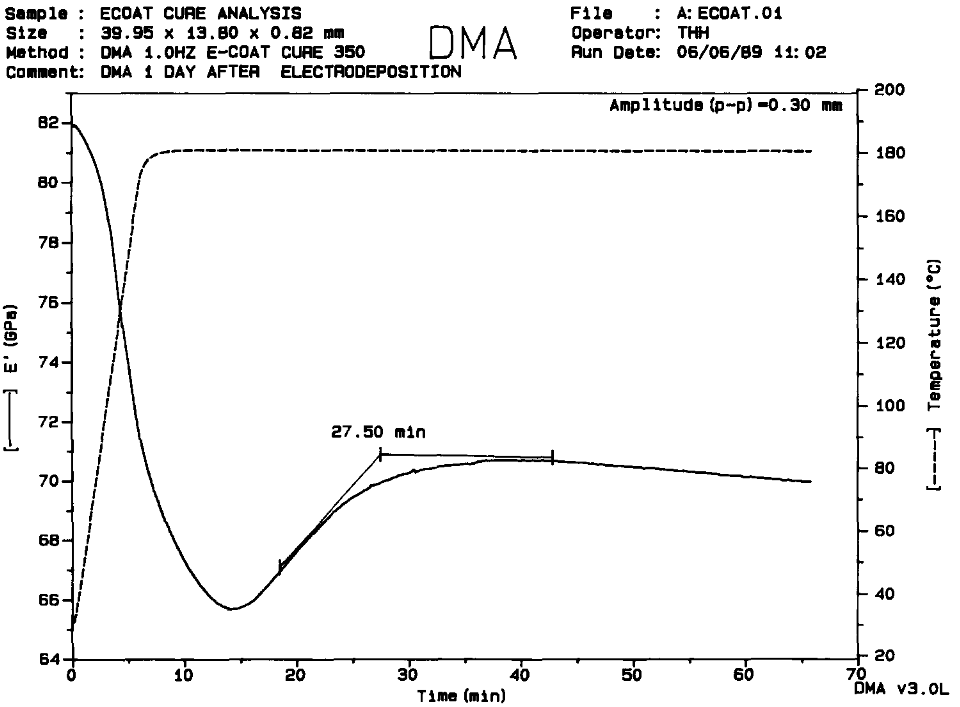

Fig. 3. Cure analysis of an E-coat paint electrodeposited on a steel substrate of thickness 0.8 mm.

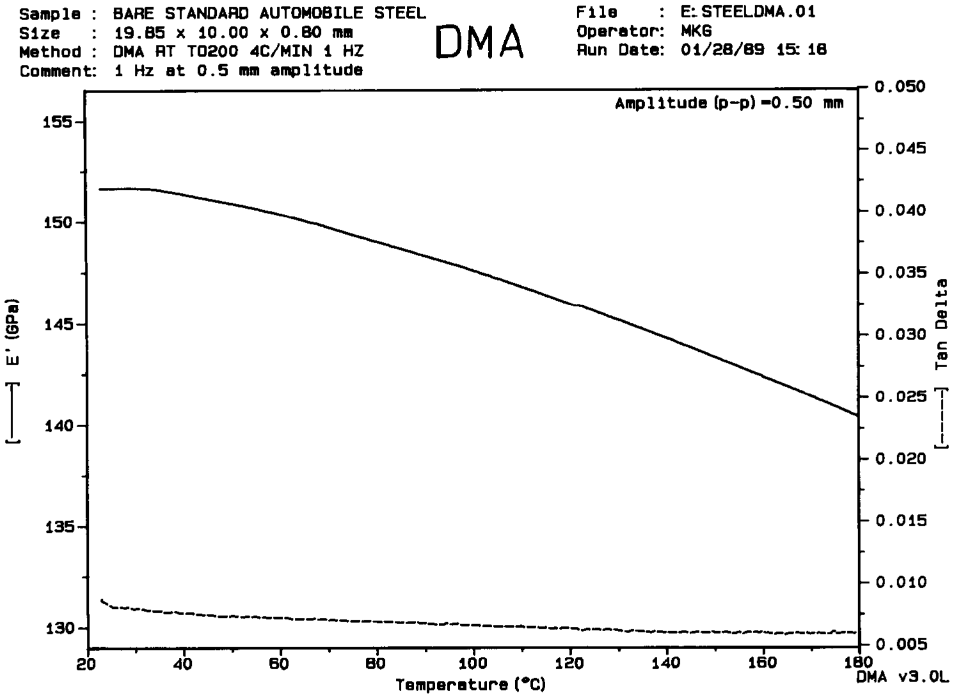

Fig. 4. DMA scan of a standard steel substrate as reference.

decrease in the viscosity of the paint, and reaches a minimum value at about 14 min. The modulus then gradually increases and reaches a constant value at about 40 min into the DMA run (i.e. after 30 min at the cure temperature). This indicates that 30 min at the cure temperature is sufficient time for the curing of this paint. The time to reach a constant modulus value depends on the temperature and type of the paint. For some paints a constant modulus value was not reached even after 60 min at 177 °C.

For a typical curing profile experiment, a 3 × 3 time–temperature matrix will be generated. This will include three temperature settings, one at the expected cure temperature, one above this and one below. For each temperature a three-bake cycle will be used, one at the normal bake cycle, one above this and one below.

The DMA run of a standard steel substrate is shown in Fig. 4. The modulus curve does not exhibit any transitions and the tan δ curve is also flat for the entire temerature range used in this study. Figures 5 and 6 show the modulus and tan δ curves for the E-coat paint cured in the DMA instrument (during curing analysis) at different frequencies. Similar tan δ versus frequency curves were also generated for clearcoat and primer coatings. The dependence of the tan δ maxima on the frequencies is shown in Table 1. The tan δ maximum increases as the frequency increases.

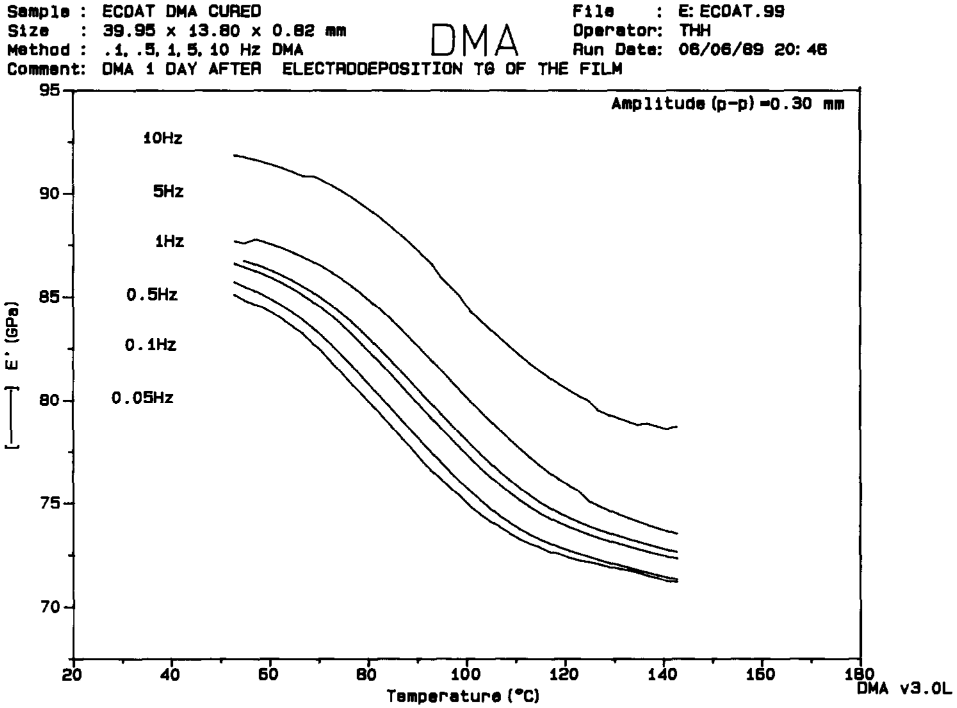

Fig. 5. Storage modulus vs. frequency for cured E-coat paint.

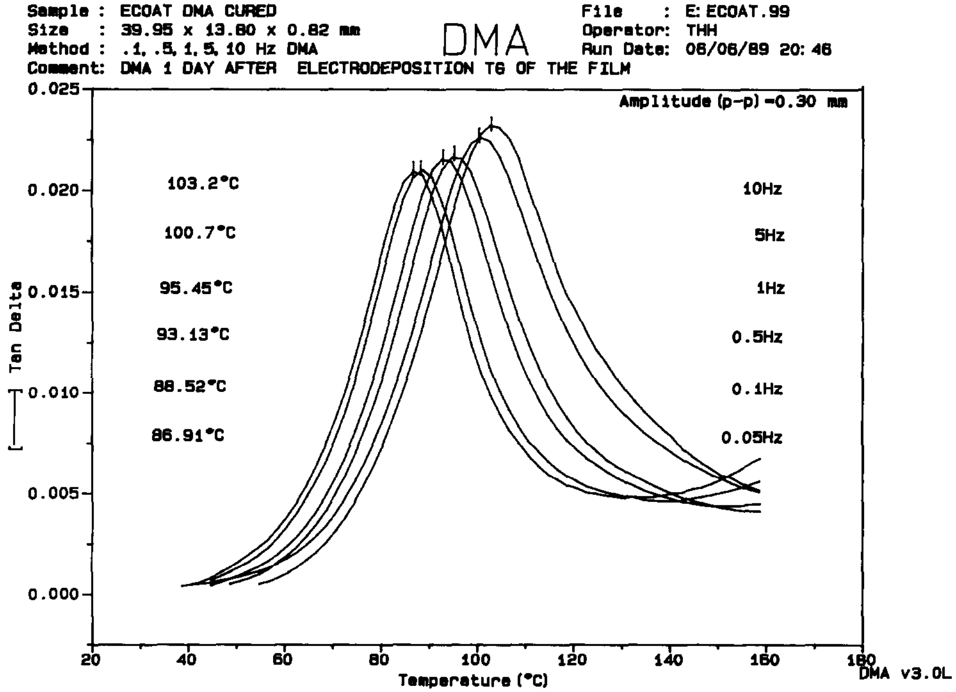

Fig. 6. Tan δ vs. frequency for cured E-coat paint.

TABLE 1

Tan δ maxima versus frequencies for E-coat

Frequency (Hz)	Tan δ Maxima (°C)
10.0	103.2
5.0	100.7
1.0	95.5
0.5	93.1
0.1	88.5
0.05	86.9

Table 2 compares the T_g values of E-coat measured by DSC and DMA at different frequencies and heating rates. It was observed that the T_g value of the E-coat depends on whether the E-coat was cured in an electric oven or inside the DMA instrument. The T_g value of an E-coat cured in an electric oven was about 15°C higher than one cured inside the DMA instrument. The difference was real and was also reproducible with different E-coat paints. Some of the possible explanations of this discrepancy are as follows.

(1) The ovens used for the curing of paints have a high air circulation, which could affect the cure and also the removal of residual solvents and therefore the T_g value of the cured E-coat.

(2) The sample temperature in the DMA instrument was significantly different from the set-up temperature. This means that if the sample was set up for a 177°C cure, the actual cure temperature at the sample might have been only around 165°C.

(3) The DMA temperature depends on both radiant and convection heating.

DMA analysis of multi-layer coatings

Figures 7 and 8 show the DMA analysis for a three layer sample in the fixed frequency and resonance frequency modes. The transitions for the paint layers are not well resolved in the resonance mode. The resonance frequency for the multi-layer sample on steel substrate was about 30 Hz.

TABLE 2

Comparison of T_g measurements by DSC and DMA

Method	Heating rate	Frequency	T_g (°C)
DMA	4°C min^{-1}	1 Hz	132.2
DMA	2°C increment	1 Hz	112.7
DMA	2°C increment	0.05 Hz	104.7
DSC	4°C min^{-1}	–	83.8

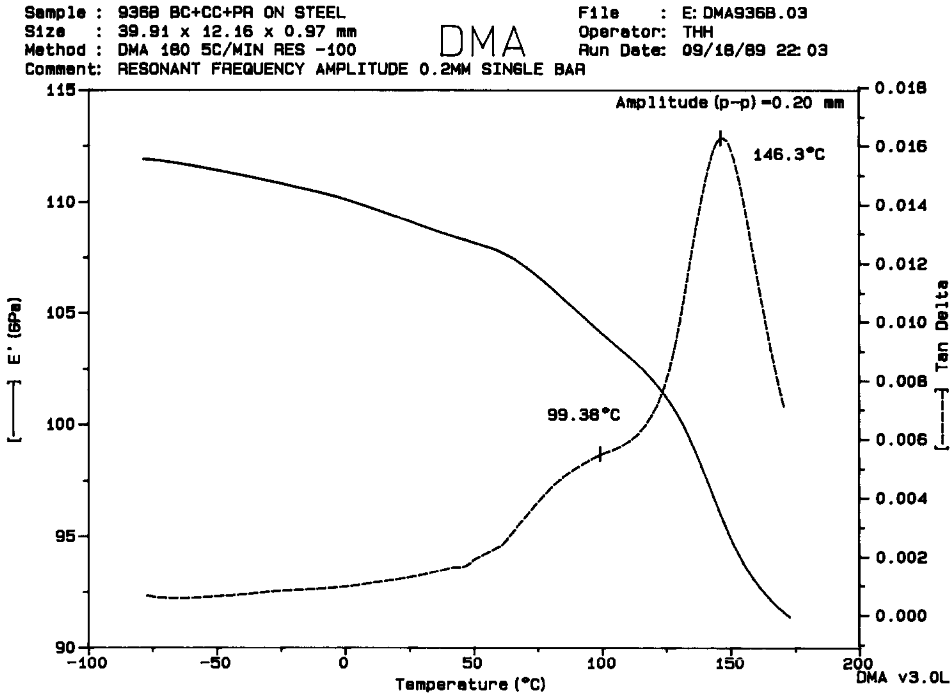

Fig. 7. Multi-layer coatings on a steel substrate in the fixed frequency mode.

As shown in Fig. 6, the higher frequency causes an upwards shift in the transition temperature. The resonance frequency depends on the sample dimensions. It is therefore difficult to obtain reproducible transition temperatures in the resonance frequency mode.

It was found that the two sample sandwich gave a stronger DMA signal. Figures 9 and 10 compare the DMA scans of sandwich samples in two configurations. The basecoat transitions were very weak and are not visible for these samples. It is evident from Fig. 9 that for configuration I the transitions for E-coat and clearcoat are well resolved. However, it was later found that the T_g values are not very reproducible. One possible explanation is that for configuration I, the clearcoat layers flow together and are therefore also dependent on the thickness of the clearcoat layer. After the DMA run, the two samples were often found to be glued together, and flow marks could also be seen on the samples in this configuration.

For configuration 0, however, as shown in Fig. 10, the transitions are broader in shape and the T_g values are more reproducible. To date we have not seen any advantage in using the two sample sandwich to obtain basecoat T_g values, because usually the basecoat peak is buried underneath the clearcoat peak and cannot be resolved even in fixed frequency mode.

Figure 11 shows the DMA run of a multi-layer sample where the basecoat, clearcoat and E-coat transitions are well resolved. In general, the

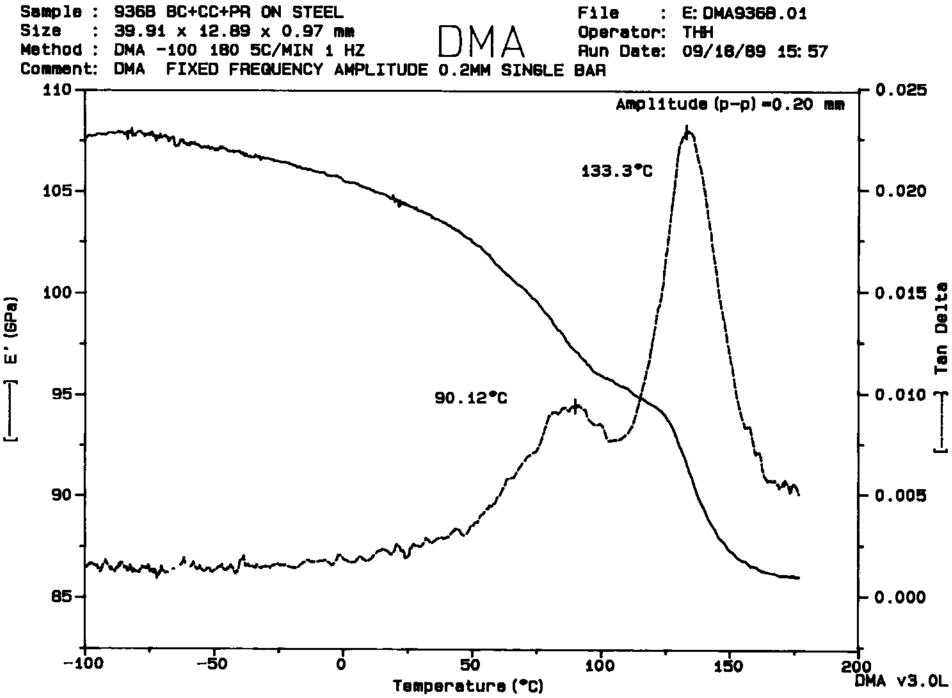

Fig. 8. Multi-layer coatings on a steel substrate in the resonance mode.

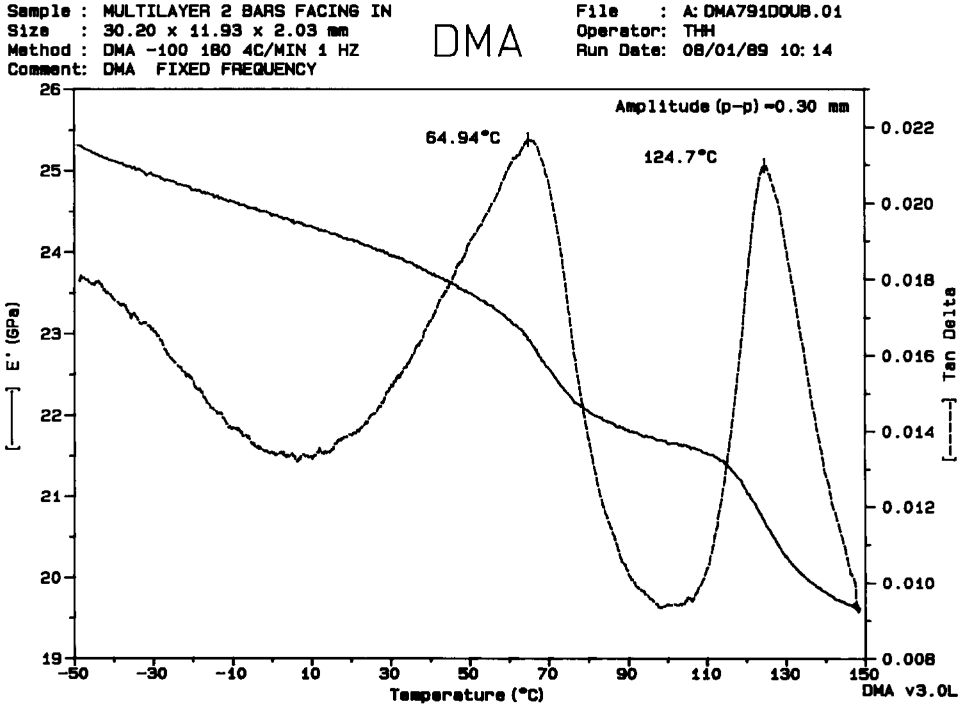

Fig. 9. Two multi-layer coatings on steel, configuration I.

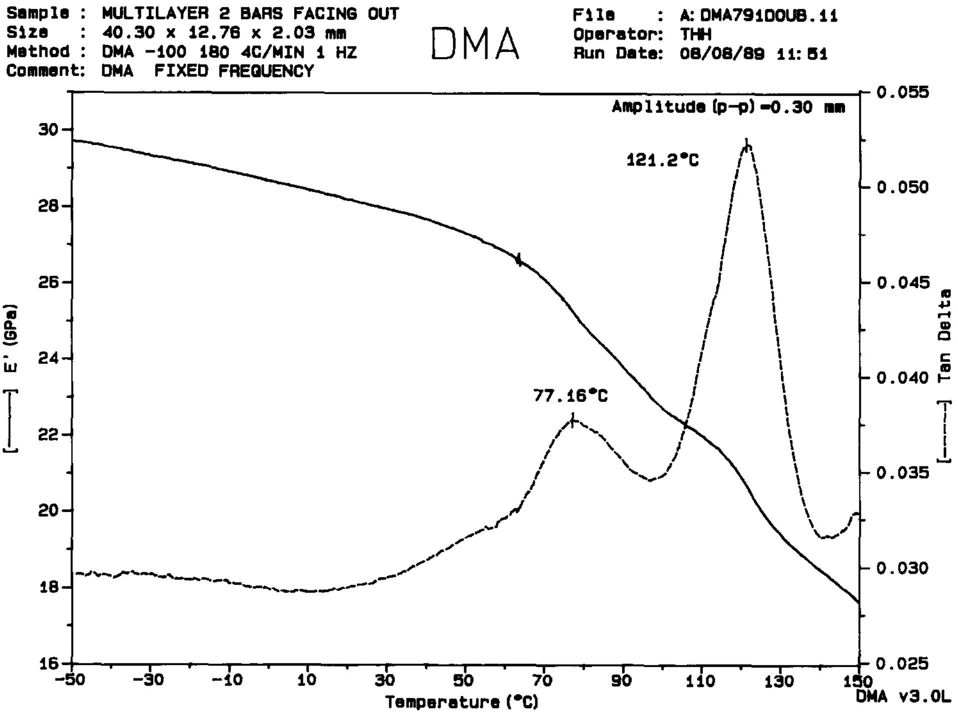

Fig. 10. Two multi-layer coatings on steel, configuration 0.

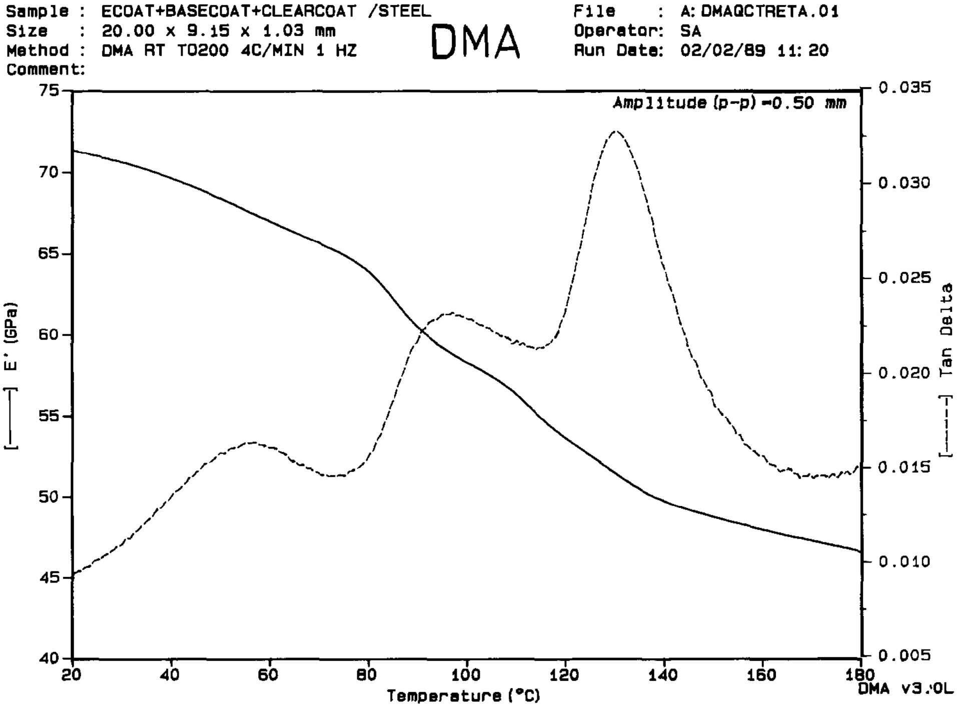

Fig. 11. DMA scan of a multi-layer sample where E-coat, basecoat and clearcoat signals were well resolved.

transitions due to the basecoat are not well resolved in the DMA scan of multi-layer samples.

CONCLUSIONS

We have demonstrated the use of DMA for the cure analysis of coatings on the standard steel substrate used for automobiles. The glass transition temperature of multi-layer coatings on the substrate were also determined by DMA without removing the coatings from the substrate. The measurement of the T_g value of the cured basecoat on the steel substrate by DMA was very difficult. It is even more difficult to determine the T_g value of the basecoat in a multi-layer coating which has a very thin basecoat layer.

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