Characterization of Coil Coatings by Thermal Analysis

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Abstract: The interrelationship between the network formation process and performance properties makes cure process studies critically important in the coil-coating industry. The objective of this work was to introduce thermal analysis into the evaluation of curing of uncured samples and in studies of the glass-transition temperatures of cured samples. Thermal analysis, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC) were used to characterize gelation and curing of three types of samples: paints, coated sheets, and free films. In addition to the generally used three-point-bending and extension geometries, a cup-and-plate geometry also was used in analyzing gelation and curing of liquid samples. These thermal analyses are suited to the purpose of characterizing coil coatings. A correlation between PMT (peak metal temperature) and measured T_g (glass-transition temperature) was found, as well as effectively distinguishing different curing conditions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2016–2022, 2003

Key words: coil coating; curing; thermal analysis

INTRODUCTION

Coil coating is a continuous and highly automated process for coating metal before fabrication. In one continuous process a coil of metal up to 1.4 m wide is unwound at speeds as fast as 90 m/min. Both the top and bottom sides are cleaned, chemically treated, primed, oven cured, topcoated, oven cured again, and recoiled for delivery. Coated coils can be produced in an endless combination of metals and finishes. In addition, they can be printed and embossed to create special visual effects. Coil-coating lines can also laminate various combinations of metals and films to metal—creating decorative and structural composites.[1,2]

This manufacturing process nevertheless presents several technical challenges. One in particular is achieving "optimum cure" of the coating system. Typical residence times in ovens are only 20–40 s, and during that time the coated substrate must be properly and evenly cured if it is to meet end-product expectations and requirements. A prepainted coil must exhibit excellent flexibility in order to withstand the often-rigorous forming operations, yet it must be hard enough to resist abrasions and the various chemicals encountered in the manufacturing process.[3] The rate of cure and its dependence on temperature and chemical conversion is important in order to predict the course of the reaction and the intermediate and final properties of the material. The end-use performance of these kinds of coatings is affected by the coating process and the coating formulation.

The physical and mechanical properties of coatings are greatly influenced by environmental factors such as light, moisture, and heat. Because coatings are viscoelastic in nature, the glass-transition temperature, T_g, the temperature at which a coating changes from a glassy and hard material to a viscoelastic one, is a very important parameter that determines the performance of the coating under variations in temperature. Thermal analysis techniques such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA) are widely used to measure the T_g of organic coatings[4–7]

The curing of a thermosetting resin is typically characterized by gelation and vitrification. Gelation corresponds to the incipient formation of an infinite network of crosslinked polymer molecules, which occurs at a fixed extent of conversion if the reaction mechanism is not a function of temperature, and it marks the transformation from a liquid to a rubbery state to a glassy state as the result of an increase in molecular weight. In other words, gelation occurs when the reaction products form a three-dimensional network. Vitrification occurs when the liquid or rubbery reacting mixture is transformed into a glassy state as the molecular weight increases. The gel time is an important factor in industrial processes because once gelation has occurred, the thermosetting system decreases its processability.[8,9]

This work was concerned with analyzing the relationships between cure evolution and the properties of the final polyester system. Such studies can assist in

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controlling network formation and in constructing structure–property relations for thermosetting mixtures. Although the mechanical properties of coatings of epoxy materials have been fairly widely studied,[10–13] polyester materials have received little attention. In this work, DMA and DSC were used to characterize the gelation and curing of different polyester-based coil coatings. Coatings were evaluated both attached to substrates and as free films. In addition, paints of different composition were studied.

EXPERIMENTAL

Methods

Dynamic mechanical analysis (DMA)

DMA experiments were carried out on a Perkin-Elmer DMA-7 unit operating with Windows-based Pyris software using liquid nitrogen cooling. Indium was used to calibrate the DMA-7 for temperature. Both thermal and isothermal scans were made, and in DMA runs the frequency for all samples was 1 Hz.

DMA is used to measure a material's storage modulus (stiffness), E', and loss modulus (energy absorption or damping), E'', over a specific temperature range. DMA is the most sensitive of the thermal analysis techniques for assessing a sample's T_g and the completeness of cure. The results are highly useful for research and development as well as for quality assurance applications.[9] However, care must be taken in reporting T_g values obtained by DMA: the transition temperature determined by DMA is not only heating-rate dependent but frequency dependent as well. In addition to heating rate and frequency, the mechanical/rheological property (E', E'', or tan delta) used to determine the T_g must be specified.[1,4,9]

The DMA technique assesses the structure and properties of solids and viscoelastic liquids via their dynamic and damping moduli and is highly sensitive in detecting changes in internal molecular mobility. A sample undergoing DMA is subjected to a sinusoidal force of known magnitude, and the resultant displacement in the sample is measured. The DMA instrument generates and controls the sinusoidal signal applied to the sample while monitoring the resulting displacement. It then analyses both signals to give results descriptive of the dynamic behavior of the sample, and it determines the sample moduli E', E'', and tan δ as functions of temperature and/or frequency. The running conditions depend on the kind and geometry of the sample.[8,9,14]

Differential scanning calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC-7 unit operating with Windows 95/NT–based Pyris software. The DSC was calibrated for tem-

perature and enthalpy responses with indium metal (156.5°C and 28.34 J/g). From 6 to 10 mg of cured sample (free films) was hermetically sealed in an aluminum pan, and all samples were analyzed in a nitrogen atmosphere.

DSC measures the heat flow into or from a sample as it is heated, cooled, and/or held isothermally. For thermosetting coatings the technique provides valuable information on glass-transition temperatures (T_g) and degree of cure.

Materials

Three types of coil coatings were studied. The samples, their preparation, and the DMA and DSC running conditions are described in the following.

Paint samples

The paint samples (Table I) were polyester-based coil-coating paints with a melamine curing agent. Three resin–curing agent compositions were investigated: 90:10, 82.5:17.5, and 75:25. The exact composition of the samples was unknown.

The properties of liquid materials can be measured by a cup-and-plate geometry. The Perkin-Elmer DMA-7 was equipped with a cup-and-plate measuring system in which a 13-mm-diameter cup was mounted at the base and a parallel 10-mm-diameter plate at the top. This measuring system enables characterization of paints and similar materials from the uncured low-modulus (liquid) state to the fully cured high-modulus state without change in the sample geometry.

The sample cup was filled about halfway, up to 2 mm; then it was placed in the instrument at ambient temperature and brought to the cure temperature as fast as the instrument allowed. The top plate was supported until the desired temperature was obtained and then lowered so that it touched the specimen but did not penetrate it. This was done by applying "floating forces," that is, static forces such that the forces cause the probe to float at the sample height. The runs were started using a dynamic force that gave amplitude of about 5 μm throughout the run. Samples were scanned at an isothermal temperature of 180°C for a maximum of 30 min.

TABLE I
Description of Paint Samples

Sample	Type	Polyester/curing-agent ratio
Paint	Polyester-based	90/10
Paint	Polyester-based	82.5/17.5
Paint	Polyester-based	75/25

TABLE II
Description of Coated Sheet Samples

Sample	Type	Curing conditions		
Coated sheet Series A	Steel substrate 0.5 mm, coating 25 μm	PMT 216*	PMT 232	PMT 249
Coated sheet Series B	Steel substrate 0.5 mm, coating 25 μm	Undercured 210°C	Properly cured 232°C	Overcured 254°C
Coated sheet Series C	Aluminum substrate 0.5 mm, coating 25 μm	Samples a and c 330°C 35 s "fast"	Samples b and d 230°C 5 min "slowly"	

* PMT peak metal temperature

Coated sheets

Dynamic mechanical measurements of the coated sheets were performed using a three-point bending geometry. The rectangular specimen dimensions were 18 mm × 4 mm. The samples for DMA were coated onto one side of a metal substrate (typically 100 mm × 150 mm) and cured at different temperatures for different lengths of times. The entire preparation was designed to simulate that of an actual coil-coating line. The thickness of the coating was about 25 μm, as in normal polyester coil-coating applications.

As described in Table II, three series of samples were prepared. In series A the samples analyzed were coated onto a hot dip zinc-coated steel substrate and cured at 330°C for different baking times. According to their residence times in the oven, the samples were labeled PMT 216, PMT 232, and PMT 249, where PMT is peak metal temperature. The samples were scanned from 25°C to 100°C at a heating rate of 4°C/min.

In series B the samples were applied over a hot dip zinc-coated steel substrate and cured at three curing temperatures: undercured, 210°C; properly cured, 232°C; and overcured, 254°C. These samples were scanned from 20°C to 100°C at a heating rate of 4°C/min.

In the last series, series C, the samples were coated onto an aluminum substrate and cured at 330°C for 35 s or at 230°C for 5 min. The samples were scanned from 25°C to 200°C at 4°C/min.

Free films

Extension was used as the measuring system in studies on the dynamic mechanical properties of free films (Table III). The dimensions of the free films were approximately 25–30 mm × 5 mm, and they were 25 μm thick. The edges of sample were carefully cut to provide an even clamping surface. The free films were scanned from −10°C to 90°C at 4°C/min.

To obtain free films of the desired quality and the desired thickness of the coating, several substrates such as steel, aluminum, and galvanized steel and several release agents such as Teflon®, silicone, and hydrochloric acid were evaluated.

In series 1 the free films were prepared by applying first a thin, uniform layer of Teflon® and then the coating over the steel substrate, Q-Panel QD-36 (Lab Products). By varying the baking time, the films were processed under three cure conditions: 210°C (undercured), 232°C (properly cured), and 254°C (overcured). The dried films were then carefully removed from the sheets. This method of preparation allowed an easy removal of the films. Another experiment was done using the same substrate and the same curing conditions but with silicone as the release agent. However, in this case the cured coating could not be peeled off the steel substrate.

In series 2 the free films were prepared by applying the coating directly over the galvanized steel substrate and curing under the same conditions as in series 1. After drying at room temperature for more than 24 h, the films were dissolved in 5% hydrochloric acid. However, the films contained pinholes and wrinkles and were brittle. The preparation of crack-free samples was difficult, and all samples were too fragile to handle when set into the probe.

For the DSC measurements free film samples on the steel substrate with Teflon® as the release agent were cut into tiny pieces and hermetically sealed in aluminum pans. The samples were scanned from 10°C to 80°C at a heating rate of 10°C/min.

TABLE III
Description of Free-Film Samples

Sample	Type	Curing conditions		
Free film Series 1	Steel substrate, Teflon® as release agent	Undercured 210°C	Properly Cured 232°C	Overcured 254°C
Free film Series 2	Steel substrate, Silicone as release agent	Undercured 210°C	Properly Cured 232°C	Overcured 254°C
Free film Series 3	Galvanized steel substrate, 5% hydrochloric acid as dissolvent	Undercured 210°C	Properly Cured 232°C	Overcured 254°C

RESULTS AND DISCUSSION

Paint samples

The cure of thermosetting resins is complicated by the interaction between the chemical kinetics and the physical properties. Near vitrification, the kinetics is affected by the local viscosity, which in turn is a function of the extent of the reaction and the temperature. Thus, the cessation of the reaction is not necessarily an indication that it is complete—the reaction may simply have been quenched because of vitrification.[15]

The gelation process occurs over a period of time, and the gel time value depends on the criterion used for its determination. Tung et al.[16] proposed a correlation between the gel point and the intersection point of the curves of storage (E') and loss modulus (E''). At the beginning, when the sample is in a liquid state, the viscous properties predominate: $E'' > E'$ and tan $\delta > 1$. In the solid state the elastic properties predominate: $E'' < E'$ and tan $\delta < 1$. At gel point $E'' = E'$ and tan $\delta = 1$. Gillham[17] investigated isothermal curing measurements, considering the gel point to the point at which the storage modulus E' reached its maximum.[15]

The curing reactions of the paint samples were rapid, and although some discrepancies were evident in the DMA plots, gel points related to the reactivity could be determined. The gel times were determined, with the use of cup-and-plate geometry, as the crossover of the elastic (E') and viscous (E'') modulus ($E' = E''$ and tan $\delta = 1$).

Paints with three polyester–curing agent compositions were investigated: 90:10, 82.5:17.5, and 75:25 (Fig. 1). First, the E' modulus was parallel to the time axis because of low crosslinking. Then the modulus increased exponentially with time, and the gel time was reached. Finally, the modulus increased still more rapidly and reached a plateau, indicating that the sample had been cured. As can be seen in Figure 1, the gel times decreased with an increase in the amount of the curing agent.
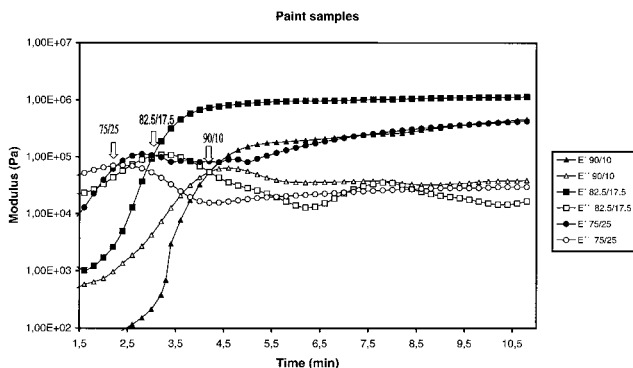

Figure 1 Curing of paints with three different polyester/curing agent compositions: 90/10, 82.5/17.5, and 75/25.
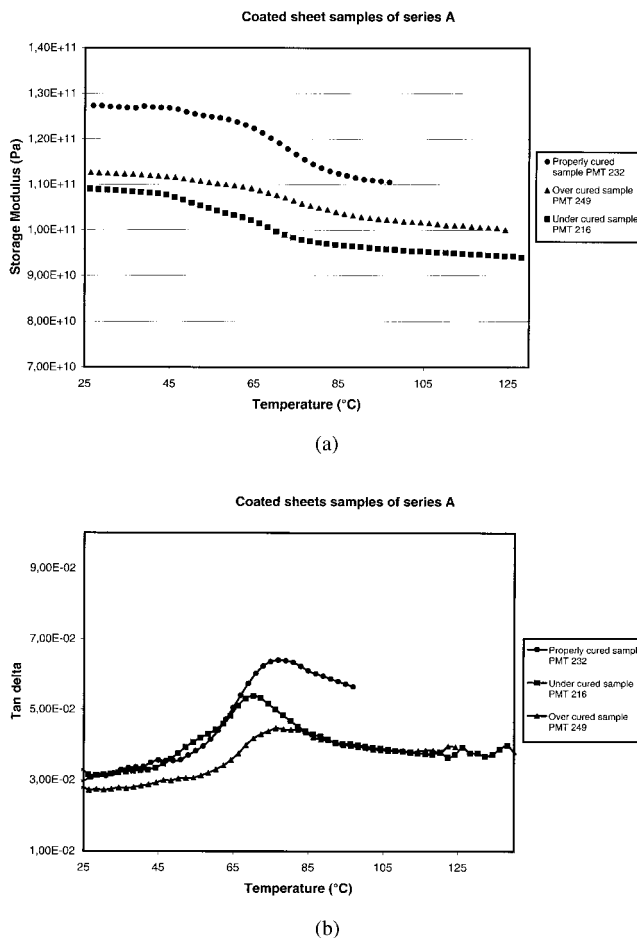

(a)

(b)

Figure 2 (a) Storage modulus and (b) tan delta curves of series A coated sheet samples.

Coated sheets

Even though the samples were very thin (about 25 μm), DMA was successfully applied for the measurement of T_g of coil coatings on a metal substrate, such as steel and aluminum sheet. Here T_g was taken as the temperature of the maximum in the tan δ plot. In some studies[17] T_g was taken as the temperature of the maximum in the loss modulus plot, and this value was closer to that obtained by differential scanning calorimetry. However, these two T_g values, maximum in the E'' and tan δ plots, can differ considerably. In our work the difference was about 8°C–10°C. The reproducibility of the measurements was good.

The E' and tan δ curves of series A samples are plotted in Figure 2(a,b). The storage modulus level at the left is typical of a coating before curing. The middle portion of the plot is the glass-transition region where E' drops sharply and both E'' and tan δ pass through a maximum. The nearly flat part of the E' plot at temperatures well above T_g is called the rubbery plateau. The height of the maximum of the tan δ peak is also sensitive to cure conditions. In many cure studies it has been noted that as cure temperature or cure
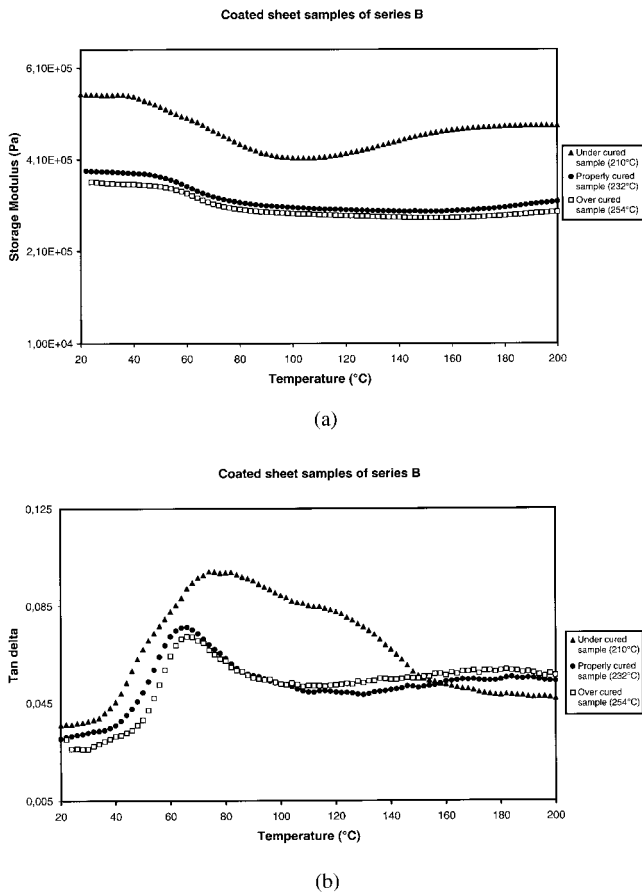
(a)

(b)

Figure 3 (a) Storage modulus and (b) tan delta curves of series B coated sheet samples.

time was increased, T_g increased, tan δ (max) decreased, and E' (min) increased.[7–9,18,19] If E' drops in the rubbery plateau, the cause could be thermal degradation or melting of poorly organized partially crystalline domain. In this study a correlation was found between PMT (peak metal temperature) and T_g: the coating with the lowest PMT value, 216, had the lowest T_g (70.2°C) and the coating with the highest PMT value, 254, had the highest T_g (80.5°C), and the coating with a PMT value of 232 had a T_g (76.2°C) between these two values.

Storage modulus (E') and tan δ plots of the series B samples are presented in Figure 3(a,b). The glass transition of the properly cured sample was observed as a large drop in the storage modulus and a peak in the tan δ response at 64.5°C; the corresponding peak of the overcured sample was at 66.2°C. These results indicate that both coatings were fully cured, as no increase was observed in the E' response above T_g. As can be seen in the storage modulus curve of the undercured sample, if the sample was even slightly undercured, an increase was obtained in the storage modulus response above T_g reflective of additional or residual crosslinking. On the other hand, the undercured sample of this study had a significantly high T_g, the tan δ

curve was noticeably broader, and the storage modulus was higher than the more crosslinked samples. This was unexpected because, as has been previously shown, when the cure temperature decreases, T_g normally decreases as well; and the sample with the low degree of cure has a narrow tan δ peak. Initially, we thought that the high value was an artifact of the sample preparation process or of calibration. However, when T_g measurements were made after calibration and on the other undercured sample (210°C), which was prepared in the same way, the results were similar: the measured T_g was 76.6°C. Thus, no real explanation was found for this phenomenon.

Figure 4(a,b) displays the DMA curves obtained with the series C samples. The plots show E' and tan δ (E''/E') as a function of sample temperature. In series C the samples were coated onto an aluminum substrate and cured "quickly" at 330°C for 35 s (sample a) or "slowly" at 230°C for 5 min (sample b). Samples a and b have the same formulation. As shown in Figure 4, the slowly cured sample b had a higher T_g (70°C) than the quickly cured sample a (66.8°C). Crosslinks reduced the available free volume, and the T_g was expected to increase with increasing crosslink density. Thus, crosslink density appears to be greater for sam-
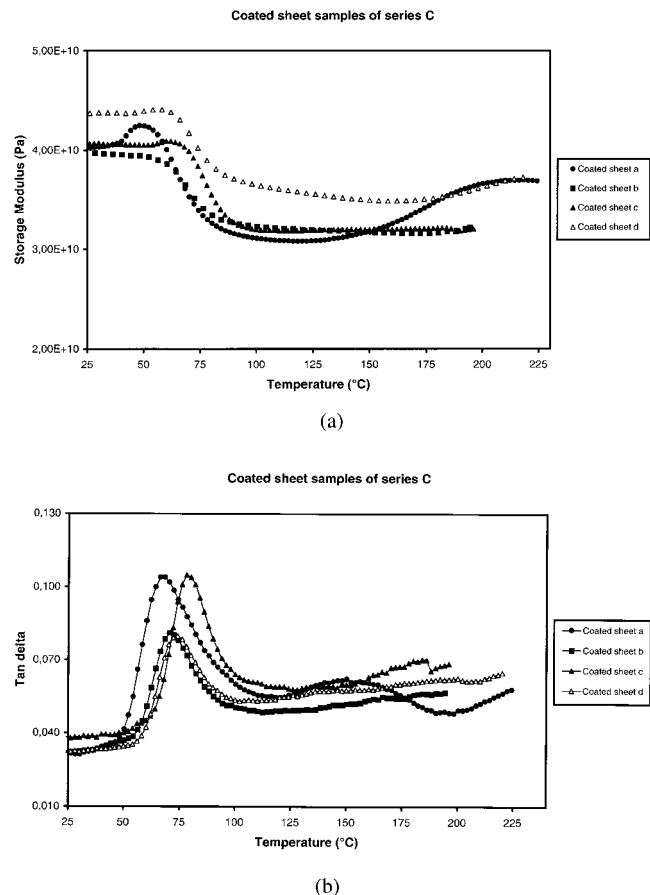

(a)

(b)

Figure 4 (a) Storage modulus and (b) tan delta curves of series C coated sheet samples.

ple b. Furthermore, sample a exhibited an increase in modulus response above T_g, indicating additional crosslinking after the rubbery plateau, at 150°C–160°C. This may suggest that some subsequent reactions may be taking place under cure conditions of temperatures higher than 330°C for 35 s.

Samples c and d have the same formulation, but the molar mass of d was higher. Because of the higher molar mass, after tan δ had gone through a maximum, the curve of sample d dipped lower than the curve of sample c. Also, E', the storage modulus, was higher for sample d.

Free films

In the free-film studies, substrates of steel, aluminum, and galvanized steel release agents of Teflon®, silicone, and hydrochloric acid were evaluated. The best films were prepared on steel substrate with Teflon® as the release agent, and only these films were analyzed by DMA and DSC. Other combinations yielded samples that were too brittle or the coating could not be peeled off from the substrate after curing.
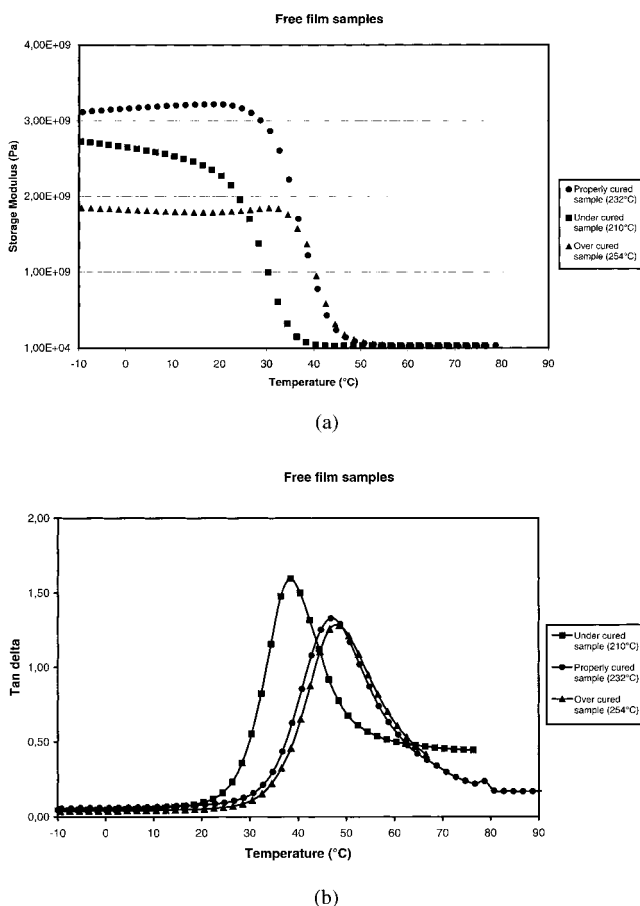

(a)

(b)

Figure 5 (a) Storage modulus and (b) curves of free films prepared on steel substrate with Teflon® as release agent.
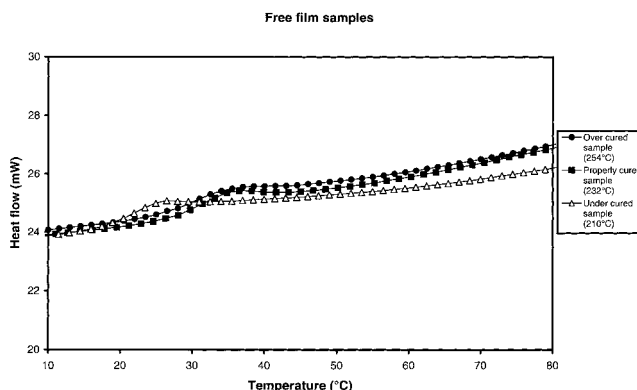

Figure 6 DSC curves of free film samples prepared on steel with Teflon® as release agent with three different cure conditions: under cured 210°C, properly cured 232°C, and over cured 254°C.

Film quality is critical in studying these kinds of samples because bubbles and other inhomogeneities affect the measurements. Certainly, the reproducibility of the free films was the best of all in the coil-coating samples. However, the preparation of free films was time consuming, and the effects of interactions between coating and substrate were lost for the films.

The thickness of the free film, which varied between about 25 μm and 40 μm, did not seem to affect the T_g value. For example, when thicknesses of the free films were 28.3 μm and 36.3 μm, the glass-transition temperatures were 50.7°C and 49.5°C, respectively.

The free films that were analyzed were prepared on steel substrate with Teflon® as the release agent and were processed as undercured at 210°, properly cured at 232°, and overcured at 254°C by varying the baking time. Figure 5(a,b) shows the DMA curve profiles of these samples around T_g. As for the coated sheets, the T_g was taken as the temperature of the maximum in the tan δ plot. It can be seen that the T_g shifts towards higher temperatures from the undercured system to the overcured system.

The same samples were analyzed by DSC, and the results are presented in Figure 6. The T_g of the undercured sample was significantly lower, but the T_g values of the properly cured and overcured samples were not clearly different. DMA is a much more sensitive technique, and as is shown in Figure 5, it can also effectively distinguish properly and overcured samples.

CONCLUSIONS

Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to evaluate the curing of different types of coil coatings. Thermal analysis provided information on crosslink density, which was difficult to obtain by other methods. DMA

also provided reliable T_g values and, equally important, indicated the breadth of the glass transition, which is related to homogeneity.

The present work has demonstrated that with DMA technique, the T_g of coil coatings can be measured *in situ* and can effectively distinguish different curing conditions. A correlation was also found between the peak metal temperature (PMT) and measured T_g: samples with PMT values of 216, 232, and 254 had T_g values of 70.2°C, 76.2°C, and 80.5°C, respectively. Similarly, in the studies on coated sheets, T_g values were indicative of the degree of curing, as T_g was shifted toward higher temperature from the undercured system to the overcured system. Furthermore, if the specimen was even slightly undercured, an increase was obtained in the storage modulus response above T_g, indicating an additional or residual crosslinking.

In addition to the analysis of cured samples, DMA can be used to analyze the curing reaction and gelation of liquid materials like paints with a cup-and-plate geometry. The gel time is an important factor to take into account at the industrial level because the processability of thermosetting systems decreases from that time onward. In this work the gel times of paint samples were found to decrease with an increase in the amount of curing agent.

References

1. Gaske, J. E. Coil Coatings; Federation of Societies for Coatings Technology: Philadelphia, 1987.
2. What is Coil Coating? http://www.precoatmetals.com/what.htm (accessed April 30, 1999).
3. Bell A. F.; Howard III, J. M. The Determination of the Degree of Cure of Polymeric Coatings on Coated Steel Coil; CTAS 7th Annual Technical Meeting; Toronto, Ontario, 1997.
4. Hill, L. W. J Coat Tech 1992, 64, 808.
5. Cadenato, A.; Salla, J. M.; Ramis, X.; Morancho, J. M.; Marroyo, L. M.; Martin, J. L. J Therm Anal 1997, 49, 269.
6. Enns, J. B.; Gillham, J. K. J Appl Polym Sci 1983, 28, 2567.
7. Diaz, I. M.; Jacquin, J. D. Modern Paint and Coatings 1998, 32.
8. Martin, J. S.; Laza J.; Morrás, M. L.; Rodriquez, M.; Leon, M. Polymer 2000, 41, 4203.
9. Hill, L. W. Mechanical Properties of Coatings; Federation of Societies for Coatings Technology: Philadelphia, 1987.
10. Hoffman, K.; Glassen, W. G. Thermochimica Acta 1990, 166, 169.
11. Harran, H.; Laudouard, A. J Appl Polym Sci 1996, 32, 6043.
12. Muzumdar, S. V.; Lee, L. J. J Polym Eng Sci 1991, 31, 672.
13. Varley, R. J.; Hodgin, J. H.; Hawthorne, D. G.; Simon, G. P.; J Appl Polym Sci 1996, 60, 2251.
14. Sichina, W. J. Characterization of Electronic Materials Using Thermal Analysis; PerkinElmer PETech-24, 1989.
15. Laza, J. M.; Julian, C. A.; Larrauri, E.; Rodriquez, M.; Leon, L. M. Polymer 1999, 40, 35.
16. Tung, C.; Dynes, P. J. J. J Appl Polym Sci 1982, 27, 569.
17. Gillham, J. K. J Polym Sci 1979, 19, 676.
18. McKetta, J. J. Thermal Analysis, Encyclopedia of Chemical Processing and Design; Marcel Dekker: New York, 1996; pp 270–278.