Study of Polyester-Based Coil Coatings By Using Thermal Analysis Methods

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The curing of polyester-based clearcoats has been studied by using thermal analysis methods. Polyester resins are used as raw materials for coil coatings. The aim of this work was to study the viscoelastic properties of coil coatings. Differential scanning calorimetry (DSC) was found to be useful in curing studies of lacquers, for example, to predict conversion as a function of cure time or cure temperature. Dynamic mechanical analysis (DMA) was used to determine the gel times of some clearcoats. The DSC measurements were done with different apparatus and software programs. This study concentrates on the use of these modern techniques to predict the curing and correlation of the results.

INTRODUCTION

In commercial coating applications, thermosets are rarely used without the incorporation of other materials, since a successful coating requires properties which cannot provide any one component alone. Usually the coatings consist of catalysts, hardeners, fillers, and additives. Catalysts and accelerators are employed to reduce the processing time. Hardeners will affect not only the reaction rate, but also the ultimate properties of the thermoset, such as its network structure, $T_{g\infty}$, and dynamic mechanical properties. Fillers are used both to provide or enhance physical properties such as modulus, thermal expansion and dimensional stability, thermal and electrical conductivity, and to reduce costs. Additives are commonly employed to enhance the thermal stability or burning characteristics of materials. Water and solvents that are part of the process can become involved in the chemistry of curing and, moreover, plasticize the cured thermoset.[1]

Polyester resins, in combination with amine resins or as polyurethane base resins, dominate the scene of coil coating paints with a share of about 60%. Polyester coatings with amino resin crosslinkers show a particularly well-balanced profile. It is not a star performer in any particular test, but has no weak points either. In the coil coating line, the coated strip is heated in an oven by hot air with temperatures in the range of 300 to 500°C. The dwell time of coil coatings is from 15 to 60 sec and as an upper limit for metal temperature is 250°C (PMT = peak metal temperature), above which organic materials may oxidize.[2] This kind of manufacturing process requires a fast curing system which presents quite a challenge in obtaining the right or actually optimum cure profile for different applications. When the coating has cured, it must be capable of forming around sharp bends, must have excellent exterior durability, and must withstand corrosion in marine or industrial environments. In addition, specific chemical resistance may be needed, and resistance to building-site damage is obviously required.[3]

Curing of coil coatings, as with coatings in general, is usually characterized by gelation and vitrification. In the thermosetting process gelation and vitrification take place during cure as a consequence of chemical reactions which convert a liquid resin-hardener mixture to a solid. Gelation corresponds to the incipient formation of an infinite tridimensional molecule. Vitrification, which usually follows gelation, entails a physical transformation from the liquid or rubbery state to the glassy state as a result of an increase in the average molecular weight and in the crosslink density of the material. At

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Table 1—Samples Studied in This Work. Polyesters Used Were S1, S2, and S3, with a Polyester/Curing Agent Ratio of 82.5/17.5 and the Catalyst Was p-TSA

Sample	S1 82.5/17.5 pTSA	S2 82.5/17.5 pTSA	S3 82.5/17.5 pTSA
AV solid/mg KOH/g	6.7	7.1	4.3
OHV solid/mg KOH/g	46	32	41
$Visc._{diluted}$/P (23°C)	18.7	26.9	16.8
M_n g/mol	3210	3760	3280
M_w g/mol	9030	9250	7840
MEL/OH-ratio	3.32	4.77	3.72
Catalyst % on binder	0.32	0.32	0.32
Catalyst/HMMM	0.018	0.018	0.018
Solid content/ %	64.2	63.6	63.3

vitrification, the chemical reaction slows down significantly.[4] The end-use performance of coil coatings is affected both by the coating formulation and the coating process; thus, information on the curing process is required to ensure that the properties of the material are optimized for a specific application. A number of articles have been published which describe curing more thoroughly and present several thermal analysis techniques, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), torsional braid analysis, dielectric analysis, and thermal stimulated current, that have been used in curing studies.[5-17]

This paper concentrates on utilizing the modern thermal analysis techniques to study the viscoelastic properties of liquid polyester-based coil coating systems. Modeling and property prediction overall in coatings formulation is not simple. Today there are several commercially available kinetic software applications for curing studies. In the present work we investigated the correlation between two different apparatus and software programs. Properties of coil coatings were studied experimentally by DSC and DMA.

EXPERIMENTAL

Materials

The samples and some of their physical characteristics are presented in *Table* 1. The table shows the amount of polyester and curing agent in the samples. The catalyst was p-toluenesulfonic acid (pTSA) and the curing agent was hexamethoxymethylmelamine (HMMM). The samples were analyzed as received from the coating industry and the exact composition of samples was unknown. The polyesters, S1, S2, and S3, differ in crosslinking density and molar mass. Also, the acid values and hydroxyl numbers of the samples differ. The catalyst on binder and the catalyst on curing agent is the same for each sample and the solid content is very similar.

Methods

DIFFERENTIAL SCANNING CALORIMETRY (DSC): Curing of thermosetting polyester clear lacquers has been studied by using differential scanning calorimeter methods. The polyester-amino resin ratio is generally in the range 90:10 to 70:30. In this study we used a ratio of 82.5:17.5. DSC measurements were done both with Mettler's and Perkin-Elmer's techniques.

The Mettler DSC 20(30) using nitrogen DSC cell purge was calibrated for temperature using indium and zinc, and for enthalpy using indium. Measurements were made by using medium pressure steel pans in order to avoid the evaporation of solvents and to separate simultaneous curing and evaporation reactions. The curing experiments were performed at three different temperatures: 150°C, 160°C and 170°C for 60 min. Samples in the range 6-20 mg were accurately weighed into the DSC sample pans which were then hermetically sealed. Some of the samples were also measured on Mettler DSC 821e and the results obtained with these two apparatus were compared.

The degree of curing and the reaction rates were calculated from isothermal DSC curves when using Mettler DSC 20. From the exothermic DSC curves, the degree of curing was calculated by dividing the enthalpy at time, t, by the total enthalpy of the curing exotherm. No residual curing exotherm was obtained. The reaction rate was calculated by dividing the peak height at a certain time by the total enthalpy of the curing exotherm and sample weight.

In the DSC measurements done by Mettler 821e the Model Free Kinetics program proposed by Vyazovkin[18-20] was used. Vyazovkin based his method in the Arrhenius equation in which the temperature dependence is assumed to reside in the rate constant. The used model-free kinetics software collects data from multiple experiments, usually three. Instead of a single point of conversion, the approach follows all points of conversion from the multiple experiments. Based on the results, predictions can then be made on how the reaction would proceed at various temperatures. Model-free kinetics program does not presume any information about the order of the reaction and thereby permits the solving of practical problems in the case of complex processes.

Another set of DSC measurements was performed using Perkin-Elmer DSC-7 unit operating a Windows™ 95/NT-based Pyris software. The DSC was calibrated for temperature and enthalpic responses using indium (156.5°C and 28.34 J/g). Six to 15 mg of clearcoat were sealed in a stainless steel high-pressure pan (part number 0319-0218). These pans eliminated the interfering effects of the heat of vaporization by suppressing the vaporization of solvents or by containing volatile reac-

Table 2—Results of Sample S3 82.5/17.5 pTSA Analyzed by Scanning Kinetics Program. Reaction Profile (20, 30, 50, 75, and 90%) as a Function of Time at Isothermal Temperatures 150° and 170°C

Conversion (%)	Isothermal Temperature 150°C	Isothermal Temperature 170°C
20	3.6 min	0.6 min
30	7.2 min	1.2 min
50	13.3 min	1.8 min
75	24.8 min	4.2 min
90	43.0 min	6.6 min

tion products. Samples were analyzed in a nitrogen atmosphere and scanned from 30° to 250°C at 10°, 15°, and 20°C / min. In addition, some clearcoats were run isothermally at 160°, 170° and 180°C for 30 min. For these isothermal runs, the cell was allowed to stabilize at chosen isothermal conditions before setting the sample. The results were calculated by using the kinetic software program. To perform the isothermal kinetics calculations, the software fits three to six data curves that have been taken at a constant temperature, to the Arrhenius relationship and thereby determines the pre-exponential factor, activation energy, and order of reaction. With this program, the behavior of the material can be predicted under isothermal conditions.[21]

DYNAMIC MECHANICAL ANALYSIS (DMA): DMA experiments were carried out on Perkin-Elmer DMA-7 unit operating a Windows-based Pyris software using liquid nitrogen cooling. The DMA-7 was calibrated for temperature using indium. Frequency scans were used in order to evaluate gelation. The samples were run over a frequency range of 50 to 1 Hz at three different temperatures: 150°, 160°, and 170°C. The cup-and-plate geometry was used, since it enables characterization of materials from the under-cured state through to the fully cured without changing the sample geometry.

RESULTS AND DISCUSSION

Curing Studies by Using Different Kinetics Programs

Sample S3 82.5 / 17.5 pTSA was measured by a different DSC apparatus and the results were processed by different kinetics programs: Mettler DSC 821e Model-Free Kinetics program and Perkin-Elmers' Scanning Kinetics program. The results are compared in the following section.

The results obtained by the DSC methods are summarized in *Table* 2 and *Figure* 1. *Table* 2 shows the obtained results of sample S3 82.5 / 17.5 pTSA calculated by Perkin-Elmers' Scanning Kinetics program. *Figure* 1 presents the results of the same sample analyzed using Mettlers' Model-Free Kinetics program. The conversion times can also be seen in *Table* 5. Scanning Kinetics program uses a multilinear regression to fit a single data curve, which has been taken at constant heating rate, in this study 10°C / min, to the Arrhenius relationship and thereby determine reaction parameters. Model-Free Kinetics program collects data from multiple experiments, usually three, as was the case in this study: heating rates were 10°, 15°, and 20°C / min.

Good correlation was found at isothermal temperature 150°C for conversions lower than 75%. At 75 and 90% conversion with Perkin-Elmers' Scanning Kinetics

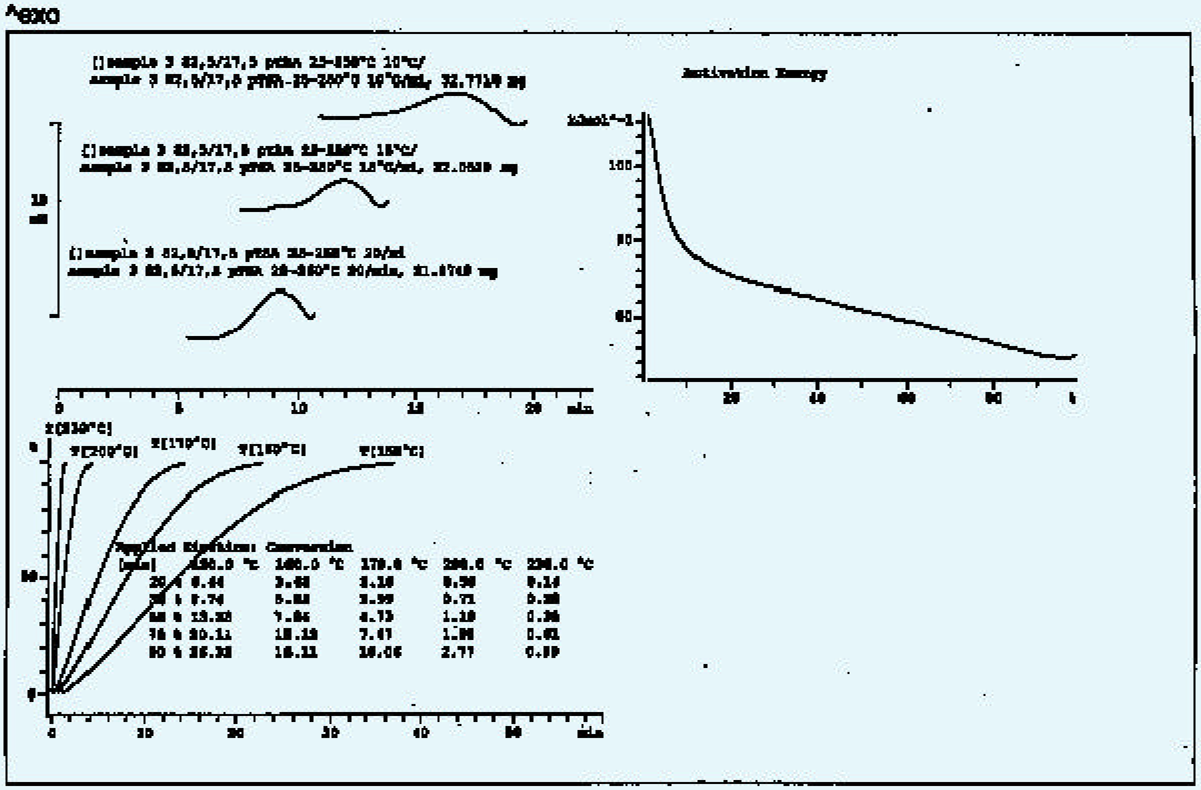

Figure 1—Dynamic scans and conversion predictions as a function of time by Mettler Model-Free Kinetics program for sample 3 82.5/17.5 pTSA.

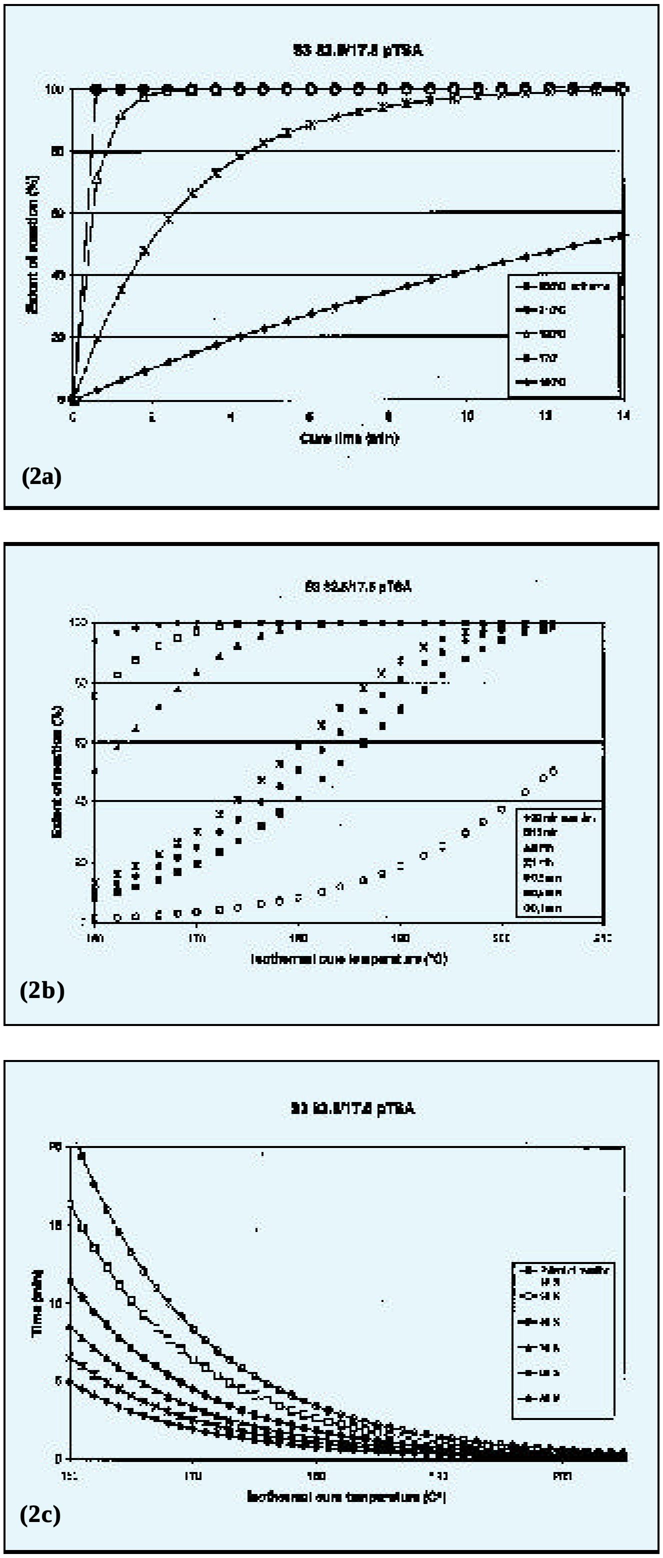

Figure 2—Curves obtained by using Perkin-Elmers´ Scanning Kinetics program for sample S3 82.5/17.5 pTSA: (a) Conversion as a function of cure time; (b) Conversion as a function of isothermal cure temperature; and (c) Cure time as a function of isothermal cure temperature.

program gave longer times than Mettlers'. Deviations observed at isothermal 170°C could be attributed to different heating rates. The Scanning Kinetics program uses only one data 10°C/min and Model-Free Kinetics program uses three different heating rates: 10°, 15°, and 20°C/min. Although the sample was the same, the experiments were done independently at different periods of time; the sample could be older and not so reactive which could also affect the measurements.

Figures 1 and 2a-c show the curves by kinetics programs: extent of reaction as a function of cure time (*Figure* 2a), extent of reaction as a function of an isothermal cure temperature (*Figure* 2b), cure time as a function of an isothermal cure temperature (*Figure* 2c), and conversion as a function of time (*Figure* 1).

Based on the dynamic measurements, the conversion predictions of sample S3 82.5/17.5 pTSA are shown in *Figure* 1. The figure shows that the higher the temperature the smaller the curing time. At temperature 230°C the conversion of 75% is reached in 0.61 min. Considering that the oven temperature in coil coating process is more or less 300°C, a curing time less than one minute should be enough to achieve a well-cured product.

As can be seen in *Figure* 2a, predicted conversion increases with temperature and the reaction is very fast at the higher temperatures 190°, 210°, and 230°C. It takes only 10 sec to reach 90% conversion. In the coil coating process the dwell time is only 15-60 sec and a fast reaction is essential to reach a desired optimum degree of cure.

Figure 2b shows the predicted extent of reaction as a function of an isothermal cure temperature and it can be seen that cure time curves 0.6, 0.8, and 1 min differ clearly from the other cure time plots. These kinds of data afford us an opportunity to evaluate the cure profile of a coating and to further develop desired properties of a final product. Roughly, in this case, 0.6-1 min curing seems to develop desired structure-property relations, whereas a shorter cure time seems to give too low a conversion and degree of cure. Using cure times higher than 5 min, the temperature used could be much lower than 200-230°C.

Figure 2c shows predicted cure time as a function of an isothermal cure temperature. These kinds of data allows for the evaluation of the optimal baking temperature.

Mettler DSC 20 vs. Mettler DSC 821e

The curing measurements and curing time predictions made with Mettlers' apparatus were mostly based on the DSC 20, but some measurements were done with the new Mettler DSC 821e and the results are compared here. The samples under study were S1 82.5/17.5 pTSA, S2 82.5/17.5 pTSA, and S3 82.5/17.5 pTSA. DSC 20 measurements were isothermal for 60 min at temperatures 150°, 160°, and 170°C. The degree of curing was calculated from the measurements by dividing the enthalpy at time, t, by the total enthalpy of the curing exotherm. The Mettler DSC 821e measurements were done in the scanning mode with three different heating

Table 3—Conversion Times at Different Temperatures for Sample S1 82.5/17.5 pTSA

	150°C		160°C		170°C	
Conversion (%)	DSC 20	DSC 821e	DSC 20	DSC 821e	DSC 20	DSC 821e
20	3.45	6.44	3.12	3.68	1.72	2.16
30	5.92	8.74	5.28	5.05	2.91	2.99
50	10.45	13.33	7.00	7.84	5.49	4.73
75	17.34	20.11	15.83	12.12	9.91	7.47
90	27.36	26.35	24.56	16.11	17.34	10.06

Table 4—Conversion Times at Different Temperatures for Sample S2 82.5/17.5 pTSA

	150°C		160°C		170°C	
Conversion (%)	DSC 20	DSC 821e	DSC 20	DSC 821e	DSC 20	DSC 821e
20	6.03	5.43	3.02	3.13	2.80	1.85
30	8.40	8.11	5.06	4.70	3.88	2.79
50	15.83	13.94	8.51	8.30	7.76	5.07
75	27.47	23.71	16.16	14.53	14	9.10
90	38.24	32.23	23.91	20.26	21.01	13.00

rates: 5°, 10°, and 20°C/min in the temperature range 25-230°C. After these dynamical measurements the Model-Free Kinetics program simulated the curing times at isothermal conditions. *Tables* 3-5 show the time to reach different conversions at different temperatures by two DSCs for samples S1 82.5/17.5 pTSA, S2 82.5/17.5 pTSA, and S3 82.5/17.5 pTSA.

The values obtained by DSC 20 were based on real measurements and the curing times were calculated manually. The DSC 821e used dynamic measurements to simulate and predict the curing times at different isothermal temperatures, and the program calculated the time to reach a certain conversion. The results obtained by these two different DSCs are in agreement, especially when the conversion is 75% or smaller, and the temperature is above 160°C. Very good similarity is seen on S3 in *Table* 5 at 75% conversion. At 150°C the curing time by DSC 20 is 25.10 min and by DSC 821e it is 24.87 min. At 160°C the values are 15.30 and 15.66 min and at 170°C 11.63 and 10.08 min. Some differences may be due to aging of sample, incidental failure in DSC-run, or uncertainty of manual calculation by DSC 20.

The effect of polyester resin on curing times can also be seen in *Tables* 3-5. In samples S1 and S2 the polyesters are slightly branched and S3 is linear. If we concentrate on conversions of 50 and 75%, the most reactive polyester is the S3 at almost every temperature and with both DSCs. Only when the temperature is 160°C and when using DSC 20 does the S2 have a slightly faster curing time than S3. As can be seen from *Table* 1, the polyester S3 has the lowest molecular weight, which could be the reason for faster curing times.

DMA Studies

In the DMA measurements, frequency scans were used to characterize gelation of a clearcoat, S1 polyester/curing agent ratio 82.5/17.5 with catalyst pTSA, at temperatures 150°, 160°, and 170°C. The properties of liquid materials can be measured by a cup-and-plate measuring system where 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 clearcoats from the uncured low-modulus state to the fully cured high-modulus state. Earlier we had succesfully investigated gelation of paint samples by the cup-and-plate system using thermal scans,[22] whereas in the present work, we used frequency scans, and in this case clearcoat sample was scanned over the frequency range from 50 to 1 Hz.

The principle of DMA is based on a study of the time dependent mechanical behavior of materials. Mechanical properties of materials are determined in dynamic modes by applying an oscillating force and measuring the material's response. The results are interpreted using fundamental relationships such as Hooke's Law (for elastic behavior) and Newton's Law (for damping or viscous behavior). These results can be normalized for sample dimensions to obtain standard reporting values such as storage modulus E', and loss modulus E'', and tan δ as a function of temperature or frequency. This method is highly sensitive in detecting changes in internal molecular mobility.[23-25]

No particular sample preparation was needed, since the clearcoat was used as delivered and the measure-

Table 5—Conversion Times at Different Temperatures for Sample S3 82.5/17.5 pTSA

	150°C		160°C		170°C	
Conversion (%)	DSC 20	DSC 821e	DSC 20	DSC 821e	DSC 20	DSC 821e
20	5.06	12.40	3.02	6.06	1.94	3.05
30	7.00	14.58	4.96	7.82	3.34	4.32
50	12.06	18.70	7.97	11.03	5.71	6.66
75	25.10	24.87	15.30	15.66	11.63	10.08
90	32.53	31.99	24.56	20.60	17.02	13.52

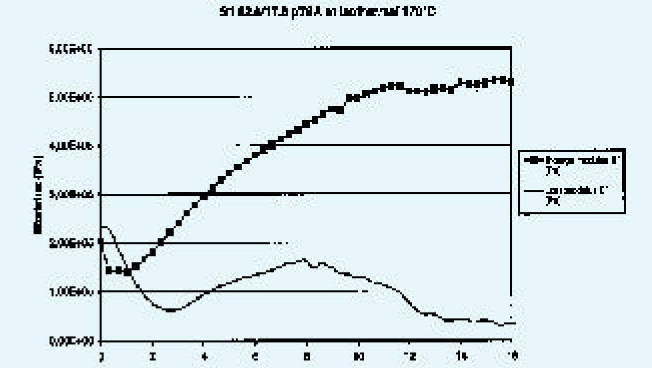

Figure 3—Storage modulus E′ and loss modulus E″ of clearcoat S1 82.5/17.5 pTSA at isothermal temperature 170°C.

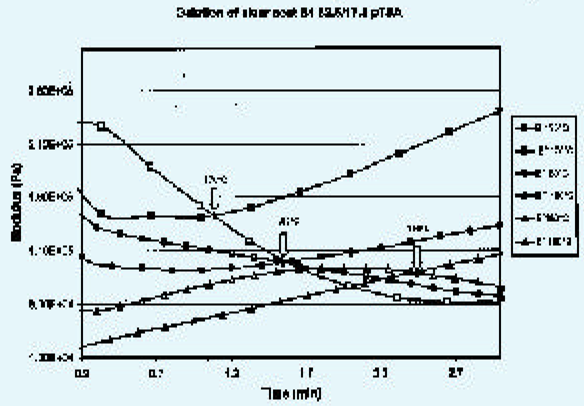

Figure 4—Variation of storage and loss modulus with time for three different temperatures: 150°, 160°, and 170°C.

ments were done as described. The sample cup was filled about half way to 2 mm. Then it was placed into the instrument at ambient temperature and brought to the cure temperature as fast as possible. The top plate was supported until the desired temperature was obtained and then lowered so that it touched the sample but did not penetrate it. This was done by applying “floating forces,” that is, static forces with such forces causing the probe to float at sample height. The runs were started using a dynamic force which gave an amplitude of about 5 µm throughout the run.

DMA plots, storage modulus (E′) and loss modulus (E″), as a function of time for sample S1 82.5/17.5 pTSA at 170°C, are shown in *Figure* 3. Gelation is one of the most important kinetics characteristics of a curing process. The gel time value depends on the criterion used for its determination and therefore it is important to specify criterion. Tung and Dynes[26] found a correlation between the gel point and the intersection point of the curves of storage modulus E′ and loss modulus E″. Gillham[27] considered the gel point to the point at which the storage modulus E′ reaches its maximum in isothermal curing studies. Lange et al.[28] investigated gelation using a torsional dynamic mechanical analyzer and found that gelation occurred when G′=G″ or tan δ=1. In this work gel times were determined as the crossover of the elastic (E′) and viscous (E″) modulus, i.e. E′=E″. *Figure* 3 shows a typical result we obtained in a frequency scan experiment. At the beginning, when the clearcoat was in a liquid state, the viscous modulus predominate and E″>E′. At the gel point E″=E′ and then E′ modulus increased with time. Finally, E′ modulus increases still more and reaches a plateau, indicating that the sample has been cured. At isothermal temperature 170°C the E′ curve begins to change to plateau after 10 min which correlates well with measurements of conversions by DSC 821e. *Table* 3 shows predicted values of conversion for this same sample: 50% at 4.73 min, 75% at 7.47 min, and 90% at 10.06 min.

Figure 4 shows modulus curves for S1 82.5/17.5 pTSA at three different isothermal temperatures. As can be seen, the gel times decreased with an increase in temperature: 150°C at 2.4 min, 160°C at 1.6 min, and 170°C at 1.1 min. This was expected since an increase of temperature leads to a faster cure reaction and gelation, indicating the incipient formation of an infinite tridimensional structure occurred earlier.

As can be concluded from the obtained DSC data, DSC measurements provide valuable information on the extent of reaction and the rate of it, but do not provide information on the gel point of the system or the resulting network structure. DMA measurements, on the other hand, do give information on the gel point and also on the network structure, crosslinking efficiency. In addition the viscosity of the reactive mixture can be measured during the crosslinking reaction. In general it seems that combined use of two or more thermal analysis techniques is the most advantageous in coating investigations. An interesting technique is an isothermal time-temperature-transformation (TTT) cure diagram, introduced by Gillham,[28] which provides a useful tool for understanding the curing and analyzing the curing processes of thermosets. With the aid of the TTT diagram it is possible to design an optimum cure cycle for desired material.[4,29]

CONCLUSIONS

DSC and DMA analyses were used to characterize the cure of a polyester resin system used in coil coating applications. The coil coating process requires a fast curing system and it is essential to find an optimum cure profile for different applications.

DSC can be a very useful tool in predicting curing times for different samples. The curing times can be easily and quite reliably obtained by any DSC apparatus despite their age and lack of modern computer programs. Nevertheless, the modern software programs proved to be very practical and time saving aids in curing studies. The same kind of results were obtained by both Mettler and Perkin-Elmer DSCs and the differences in the results were probably due to the different heating rates and aging of the sample. However, the results were in good agreement in the predicted conversion range 20-75%. Different polyester types were also compared and the S3 was found to be the most reactive one. It gave the fastest curing time at every temperature at conversions 50 and 75%.

By using the DMA technique, liquid samples like clearcoats can be analyzed with cup-and-plate geometry. Gelation cannot be observed directly by techniques sensitive only to the chemical reaction, such as DSC, whereas DMA is capable of measuring and estimating the gel point.

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