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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

CHARACTERISATION OF POLYURETHANE COATINGS USING THERMOANALYTICAL TECHNIQUES

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Abstract

A two-pack polyurethane coating was analyzed using thermoanalytical techniques. The curing reaction, monitored using pressure differential calorimetry (PDSC), rheometry and dynamic mechanical analysis (DMA) shows the temperature dependency of activation energy and hence rate of curing. In-situ ATR-FTIR shows the formation of urethane linkage over time. The decomposition behavior carried out under non-isothermal mode using thermogravimetric analysis (TGA) shows bimodal behavior. The activation energies of the initial step (10% decomposition) from both iso and non-isothermal experiments are in very good agreement with each other. The use of dynamic mechanical analysis (DMA) shows the difference in glass transition behavior (T_g) and elastic modulus (E') due to the different state of cure. Also the coating exhibits a very broad loss modulus peak (E'') indicating higher energy dissipation with deformation.

Keywords: activation energy, curing, polyurethane coating, thermoanalytical techniques

Introduction

Automotive sealing parts need a specific coating to obtain low friction, high abrasion resistance and release properties. Polyurethane (PU) coating is an attractive coating for the automotive industry because of its excellent properties. These properties, for example, include dimensional stability, adhesion to various substrates, resistance to chemicals, solvents, water, abrasion resistance, thermal stability, flexibility and toughness [1, 2]. PU can be used as a tailor made coating in almost every area of surface protection. However, in all cases, the excellent performance results primarily from the formation of crosslinks during cure. Variation in the performance of the coating is often due to improper curing. While a number of factors such as the reactivity and stoichiometry of the reactants can influence the extent of the crosslinking reaction; the cure time, and temperature finally control the transformation of viscous liquid to an elastic gel. The process of curing defines

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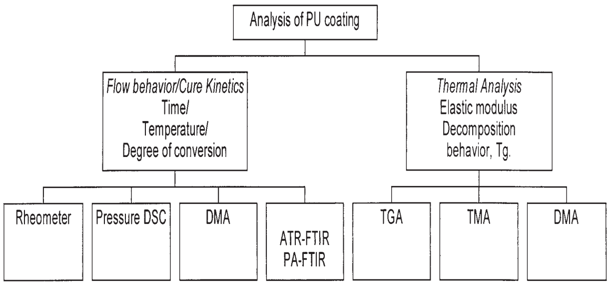
the properties of the finished coating material. In addition, the progress of the curing governs the flow properties of the final coating material, determines the cycle time required for economic processing and defines conditions that deteriorate the properties of the crosslinked structure. Reaction rate, kinetics of cure, and state of cure are, therefore, key aspects of understanding and controlling the coating performance [3]. Also the kinetics of cure allows one to develop a time-temperature-degree of conversion profile for a particular coating to assess its usefulness and relative importance of the different process parameters leading to the final product. Because of the interrelation of flow parameters and cure characteristics to performance, the rheological and thermal characterisation of this coating are crucial to the product development. In the present study, a two-pack polyurethane coating [1, 2] was characterized by thermoanalytical techniques. Despite the extensive use of this material in the automotive industry, there are few reports on the rheological and thermal behavior or the cure characteristics of this material [4]. Recently Crawford *et al*. [5] reported the thermal characterisation of a novel PU coating for military application. However, they mainly determined the performance and durability using dynamic mechanical analysis (DMA).

Thermal analysis (TA) is a rapid, cost-effective means for understanding the interrelationship between coatings synthesis, formulations, and processing and end-use performance. TA comprises a broad group of techniques used to measure changes in material properties with change in temperature [6, 7]. While a single thermal analysis technique can adequately characterise a coating's behavior, it is always important to check the validity of such characterisation by complementary techniques. Also relying on a single result can lead to serious errors in the interpretation of the data. In coating characterization, equipment such as differential scanning calorimetry (DSC), thermogravimetry (TGA), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) are very useful to define intrinsic properties, processing properties, and product performance. Intrinsic properties such as glass transition (T_g) and elastic modulus arise from the physical and chemical structure. DMA is a useful tool to characterise those properties. As physical properties are related to the extent of cure, the energy release associated with curing is important and meaningful to determine. DSC is instrumental to determine not only the energy associated with curing but also the reaction kinetics. In particular, pressure DSC (PDSC) applies to those systems, where solvent emission causes problems in the measurement and analysis. The other techniques such as rheometric study and infrared spectroscopy also can provide kinetic information on curing.

Experimental

Materials

A two-pack polyurethane coating was formed from a stoichiometric mixture of diol and diisocyanate(A:B=7.15). The component A is based on various polyester polyols (ratio 1:1:0.2) such as linear and branched polyesters (Repol 560 and 650 supplied by Townsend Chemicals, Australia) and Desmophene A450 (polyacrylate) supplied by Bayer, Australia. Approximately, 13.6 g of component A was mixed with 1.9 g of diisocyanate (component B - Desmodur L75 based on trimethylol propane and toluene diisocyanate, supplied by Bayer, Australia) with vigorous stirring at room temperature. Methyl-ethyl ketone (MEK) was used as solvent. The rate of reaction was mainly controlled by cross-linking reaction between the two functional groups represented by the symbol A and B. These two react with each other to form a covalent crosslink, A-B. Great care was taken to ensure that water was not present in the non-aqueous, two-component coating formulations due to its undesirable reaction with isocyanate [8, 9]. The formation of the polyurethane was then studied using various thermal and spectroscopic techniques. For cured coating analysis, the coating solution was properly cured at ambient temperature over 7 days. The coating was analyzed using various thermal techniques. The outline of the work is shown in Scheme 1.



Scheme 1

Methods

Reaction kinetics

Curing behavior was monitored under isothermal and non-isothermal conditions by various techniques.

Rheometric study

A Rheometric SR-5000 Controlled Stress Rheometer (Rheometric Scientific, USA) was used to study the rheological properties and curing of the coating solutions. A torque induction motor applies a sinusoidal or linear stress to the sample through the upper plate. The sample deformation is monitored by the deflection of the upper plate using an optical encoder. Analysis of the applied stress and resultant strain enables the calculation of various rheological parameters. A 40 mm cone and plate geometry was used for all measurements. The temperature was maintained constant using a Peltier element. Flow behavior was characterised at different temperatures and various shear stresses. The influence of solvent evaporation rate on the viscosity was also observed.

DSC

Cure characteristics of the coating were evaluated by using PDSC. The experiment was conducted using DSC 2920 from TA Instruments USA. The advantage of using PDSC at

500 psi is to suppress the solvent volatilization from coating. A weighed amount of sample prepared in a hermetic pan covered by a lid with a laser-drilled hole was heated at a constant rate in nitrogen atmosphere. The measurement was carried out under nitrogen flow (50 ml min^{-1}) from room temperature to 325°C at different heating rates (10–30°C min^{-1}). The exotherm peak area in J g^{-1} was used to measure the heat of curing (ΔH) [7]. All the runs were in triplicate.

FTIR analysis

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was carried out using Nicolet Magna Spectrometer (Model 750) using a trough ATR cell, at a resolution of 4 cm^{-1}, 256 scans over different time periods to analyze the chemical structure as curing progressed. To follow the completion of reaction, photoacoustic FTIR was done on cured samples after a week using same conditions at a mirror velocity of 0.15 cm min^{-1} and carbon black as reference.

Intrinsic properties

TMA

Thermomechanical analysis was used to measure elastic modulus of the PU coating. Thermomechanical analysis was performed at room temperature in TMA 2940 from TA Instruments. The indentation probe was used both with a variable load from 1–5 g at room temperature. The probe zero was adjusted after the sample was cooled.

DMA

DMA is a powerful tool for characterising the curing processes in thermoset materials. Dynamic mechanical analysis was carried out on the coating in DMA 2980 (TA Instruments) operating in compression mode under isothermal condition at different temperatures (150–180°C) to evaluate the cure kinetics. Sample was always placed on an inert substrate (cured rubber). Glass transition temperature and elastic modulus of cured coating film were measured under tension mode from –150 to 100°C at a frequency of 1 Hz, at 0.08% strain amplitude with a programmed heating rate of 3°C min^{-1}. Liquid nitrogen was used to achieve the subambient temperature for glass transition measurement.

Thermal stability and decomposition kinetics

TGA method

Thermogravimetric analysis was carried out using cured polyurethane coating under isothermal and non-isothermal conditions to analyse the decomposition behavior. Thermogravimetric analysis of the samples was conducted using a TGA 2950 thermal analyser (TA Instruments) connected to a Thermal Analyst 2200 Controller using conventional (heating rate) operating from room temperature to 600°C at different heating rates (5–20°C min^{-1}). In all analyses a nominal 20 mg sample was used, under a nitrogen atmosphere at a flow rate of 50 ml min^{-1}. The inert atmosphere was maintained from 30° to 500°C to monitor the mass loss of oil and polymer with temperature. The onset of degradation, the mass loss due to different ingredients and the residue remaining were evaluated. The temperature, at which the rate of mass loss (T_{max}) is at maximum, was evaluated from the differential thermogravimetry curves. The decomposition kinetics was carried out using the software based on Flynn and Wall method. The isothermal work was carried out at different temperatures from 270 to 310°C over prolonged time under nitrogen atmosphere. The kinetics of decomposition were calculated using Arrhenius equation.

Results and discussion

Rheometric analysis

Rheometric analysis was carried out to investigate the effect of temperature and shear stress on the flow characteristics and viscosity of the coating. The influence of solvent evaporation rate on the viscosity was also observed. Changes in viscosity result from changes in film thickness. Achieving consistent result requires maintaining the viscosity of the coating, which in turn, is controlled by the volatility of the solvents. Successful use of the coating in production line requires the coating to be very stable.

Solvent evaporation effect

The influence of solvent evaporation rate on the viscosity was observed by monitoring the flow behavior of the coating solutions over different time periods. The flow behavior was characterized at different temperatures applying various shear stresses in the range of 0.06 to 100 Pa and monitoring the sample deformation. Figure 1 shows the effect of shear stress on apparent viscosity at room temperature after different initial wait period. In all cases, the viscosity is very low and it exhibits a shear-thinning behavior. At this condition, no onset of cure is detected. The shear rate range examined covers the shear rate region of dipping operation (which will give indication of

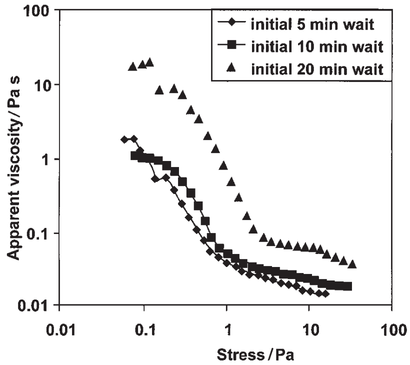


Fig. 1 Plot of apparent viscosity *vs*. shear stress for PU curing

the flow behavior during coating by dipping). However, because of the low viscosity it was very difficult to perform the high shear viscosity measurement similar to the coating spraying operation.

Effect of temperature

Oscillatory time sweep measurements were carried out under isothermal conditions at 0.5 Hz frequency to monitor the cure behavior and the elastic and loss moduli at various temperatures. Figure 2 shows the influence of temperature on shear modulus over time. At temperatures too low to initiate cure the viscosity rises very slowly with time. As temperature increases solvent loss occurs rapidly as seen from the steep slope indicating that the reaction rate is faster at high temperature. It is interesting to note that temperature has effect on the initial viscosity of the solution. However, the relative viscosity curves in the plot shows that the rate and degree of mechanical cure vary dramatically with the cure temperature. At higher temperature, skin formation is observed. Temperature sensitivity of the solution is higher as the waiting period increases. The kinetics of the reaction is also followed from this oscillatory sweep experiments.

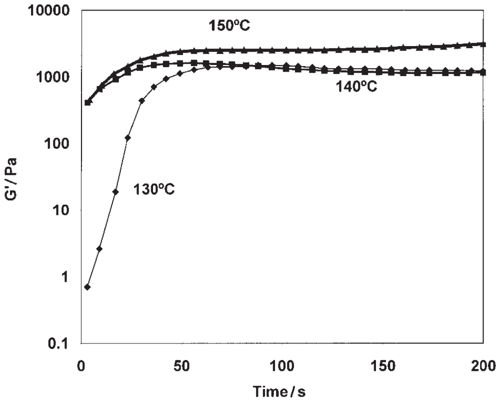


Fig 2 Dynamic storage modulus *vs*. time at various temperatures (cure characteristics)

Attenuated total reflectance (ATR) and photoacoustic (PA) FTIR spectroscopy

In-situ curing at room temperature was monitored using trough ATR liquid cell. The different spectra shown in Fig. 3 display the change in various functional groups of the PU coating while curing progressed over time. Table 1 shows the assignment of various peaks from various spectra obtained over different time period. Absorbance bands for reactive functionalities, which have increased or decreased during the reaction, are compared to the absorbance bands corresponding to non-reactive and hence unchanging bands. FTIR spectroscopy of the coating was also done over different time period. As shown in Fig. 3, the isocyanate peak (2272 cm^{-1}) and the hydroxy peak (3300 cm^{-1}) decrease and the urethane carbonyl (1703 cm^{-1}) and NH stretcth (3300–3340 cm^{-1}) increase with time as the reaction proceeds. A large absorbance at 2272 cm^{-1} due to –NCO functionality observed in the freshly prepared sample gradually decreases over time (3, 48 and 51 h) as curing progresses. The normalised absorbance as a function of time can be used to obtain the degree of conversion at room temperature at any time *t* using the normalised initial and final absorbances. The peak at 2976 cm^{-1} is found to remain unchanged over the time. The photoacoustic spectrum done after 7 days (Fig. 4) shows strong peaks due to –NH stretching and urethane carbonyl at 3330 and 1703 cm^{-1} indicating completion of the curing reaction.

Table 1 Peak assignment from FTIR spectra for PU coating

Cure time/h	Frequency/cm^{-1}	Relative intensity[a]	Assignment
0	2272	m	–(NCO)
	1703	vs	γ(C=O)bonded
	1367	m	w(CH$_2$)
	1170	s	γ(C–O–C)
	762	w	$\gamma(-\underset{\underset{\textstyle O}{\vert}}{C}=O)$
3	3500	w	γ(N–H) free
	3300	w	γ(N–H) bonded
	1703	vs	γ(C=O) bonded
	1595	m	γ(C=C) ring
	1538	m	δ(N–H)+δ(C–N)
	1367	m	w(CH$_2$)
	1170	s	γ(C–O–C)
	762	w	$\gamma(-\underset{\underset{\textstyle O}{\vert}}{C}=O)$
48	3300	m	γ(N–H) bonded
	1703	vs	ν(C=O) bonded
	1595	m	ν(X=X) ring
	1538	m	δ(N–H)+δ(C–N)
	1367	m	w(CH$_2$)
	1170	s	ν(C–O–C)
	762	w	$\gamma(-\underset{\underset{\textstyle O}{\vert}}{C}=O)$

[a] w – weak, m – medium, s – strong, vs – very strong.
ν – stretching , δ – bending , γ – out of plane bending and w – wagging

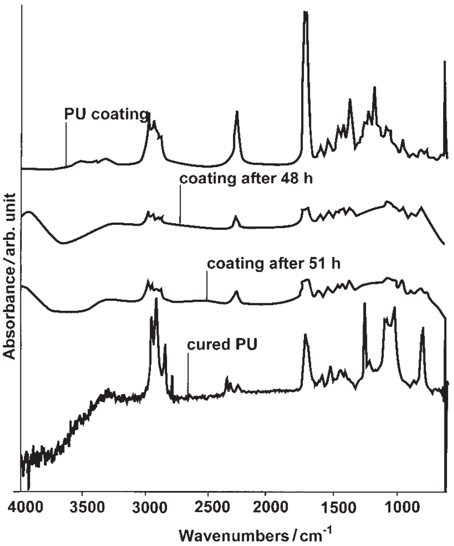


Fig. 3 PU curing study by ATR-FTIR over different time

Thermal analysis

DSC, DMA and rheometer cure kinetics

The kinetics of PU curing was monitored using DSC, DMA and rheometry. The kinetic results from different techniques allow one to gain insight into the chemical and physical factors affecting the curing process. PDSC was used at different heating rates of 10, 15, 20 and 30°C at 500 psi nitrogen to characterize the curing reaction of PU coating. Figure 5 shows the PDSC curves of non-isothermal curing of PU coating at different heating rates. The enthalpy of curing (ΔH) is found to increase with heat-

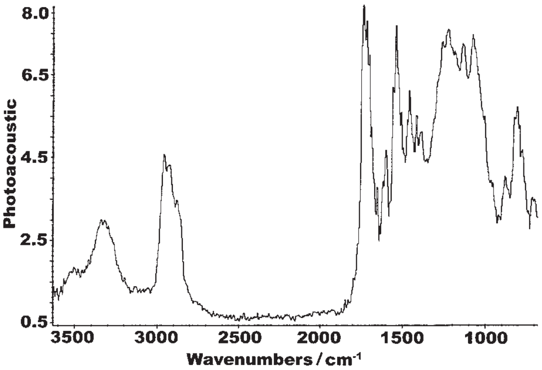


Fig. 4 Photoacoustic spectra of PU after 7 days

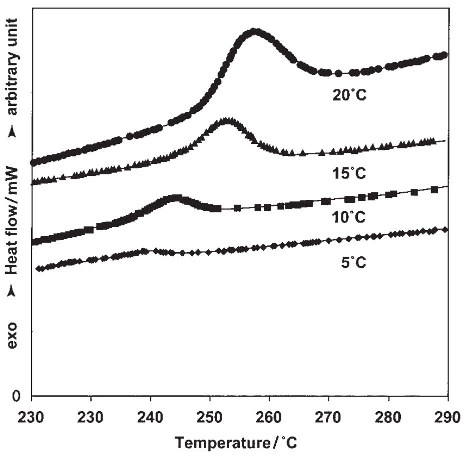


Fig. 5 Pressure DSC curves for PU curing

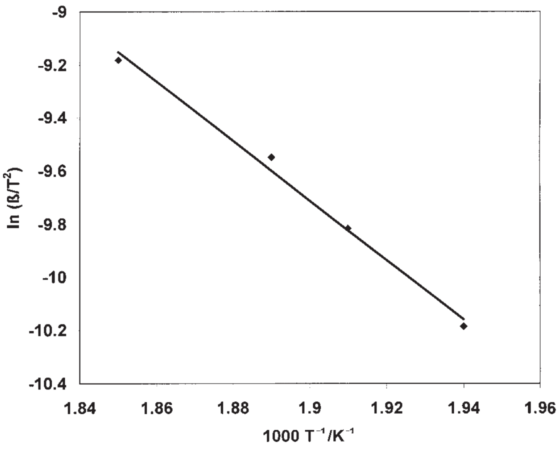


Fig. 6 Kissinger's plot of ln β/T^2 *vs.*$1/T$

ing rate. At 15°C min^{-1}, the ΔH value is 8.4 J g^{-1} whereas at 30°C min^{-1}, the value is found to be 16.3 J g^{-1} (almost doubled). A number of techniques have been developed for measuring the kinetics of chemical reaction from DSC data [7]. However, each method uses the rate of heat evolution as the computational parameter assuming that the reaction is not autocatalytic and has one rate determining step, and that the rate is unaffected by changes in the reactant concentration. The non-isothermal curing kinetics was calculated using Kissinger's model (with the assumption that peak temperature corresponds to the temperature of maximum reaction rate) as shown below:

$$\mathrm{d}\log(\beta/T_\mathrm{p}^2)/\mathrm{d}(1/T_\mathrm{p})=-E_\mathrm{a}/2.303R \qquad (1)$$

where β is the heating rate in kelvins per minute and T_p is the exotherm peak temperature. A plot of the numerator *vs*. the denominator of the left hand side expression at several DSC scans obtained at several heating rates is shown in Fig. 6**.** This gives a straight line with the slope $-E_a/2.303R$ from which the activation energy was calculated and found to be 94.4 kJ mol^{-1}. The activation energy of PU curing from different measurements is shown in Table 2.

Table 2 Kinetic parameters for PU curing and decomposition by different methods

Techniques used	Activation energy/kJ mol^{-1}		
	Reaction kinetics	Decomposition/10%DOC	
DSC	94.4		
DMA	77.59		
Rheometry	23.19		
TGA	–	isothermal	non-isothermal
		108	110

While the DSC monitors the heat flow into and out of the sample during curing process, the DMA measures the modulus or rigidity on progress of cure. DMA is very unique to correlate chemistry, morphology and performance properties. Thus the DMA and rheometer kinetic results are sensitive to volatilization of solvent, viscosity, functional reactivity, molecular mass between crosslinks, and backbone rigidity. The increase in relative modulus or shear viscosity is related to the fractional conversion or degree of cure F (t, T) using the following equation:

$$F(t,T)=[G(t,T)-G_1]/[G_2-G_1] \tag{2}$$

where G_1, $G(t, T)$, G_2, are the relative moduli at the onset of cure, at a given time and temperature during curing and after curing respectively. Assuming that the curing follows the general nth order rate expression:

$$\mathrm{d}F/\mathrm{d}t(t,T)=k(T)[1-F(t,T)]^{\mathrm{n}} \tag{3}$$

where n is the order of reaction. The temperature dependence of the rate constant is given by the Arrhenius expression,

$$k(T)=A\exp(-E/RT) \tag{4}$$

where A (s^{-1}) is the Arrhenius frequency factor, E (kJ mol^{-1}) the activation energy and R is the gas constant.

The activation energy from DMA is found to be 77.5 kJ mol^{-1}. It must be pointed out that the rheometer curing was carried out from 130 to 150°C whereas DMA from 160 to 180°C and PDSC under non-isothermal mode with peak maxima from 240 to 270°C. Generally, the activation energy is a measure of the rate of the reaction and increases with temperature. The present evaluation of the reaction kinetics using DMA, PDSC and rheometer shows that the kinetic data do not match as each method is sensitive to different physical events.

Since viscosity increases with cure, cure rate becomes limited by diffusion of functional group rather than their inherent activities. In general, chemical reactivity and the diffusion are equally important during curing at low temperature due to low segmental mobility. Thus, E_a value and hence the rate is lower while the curing was done using rheometer. The E_a value by different methods follow the order:

$$E_{\mathrm{a\ PDSC}}>E_{\mathrm{a\ DMA}}>E_{\mathrm{a\ Rheometer}}$$

Decomposition kinetics

TGA

In general the physical and mechanical properties of coating are greatly influenced by environmental factors such as heat, light and chemicals etc. TGA can be used in monitoring the compositional analysis and studies of thermal stability of polymeric coating. It measures the sample mass change as a function of time or temperature. Changes in mass can be associated with desorption, absorption, sublimation, vaporization, oxidation, reduction, or decomposition. In a typical non-isothermal run the sample was heated from room temperature to 600°C at a heating rate 10°C min^{-1} (Fig. 7) under nitrogen atmosphere (50 ml min^{-1}). The $T_{\max}$ corresponding to the maximum mass loss is found from the DTG. It can be seen that the degradation of polyurethane occurs in two stages. This is due to two consecutive reactions occurring during the composite decomposition of PU. The first step is the decomposition of weaker chains of PU. The active species generated in this stage promote further degradation of urethane link. The degradation starts at about 250°C with an initial loss of (3.25%) followed by the medium component occurs at 333°C (34.76%), and by the degradation of the main components at 432°C (44.09%). It is clear that the decomposition does not involve independent reactions rather two consecutive reactions. The weighting factor due two major decompositions to the total percent decomposition can then be written in the form of $\alpha=x\alpha_1+y\alpha_2$ where x=35%, y=44%. And the remaining mate-

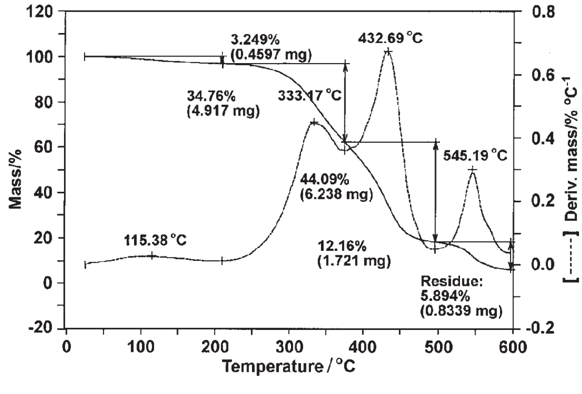


Fig. 7 Non-isothermal TGA at 10°C min^{-1} heating rate

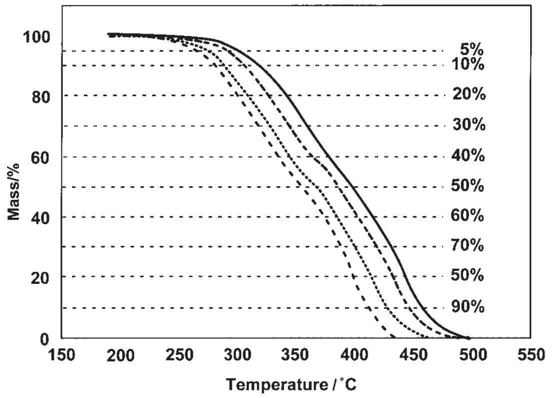


Fig. 8 Mass loss% at different heating rates

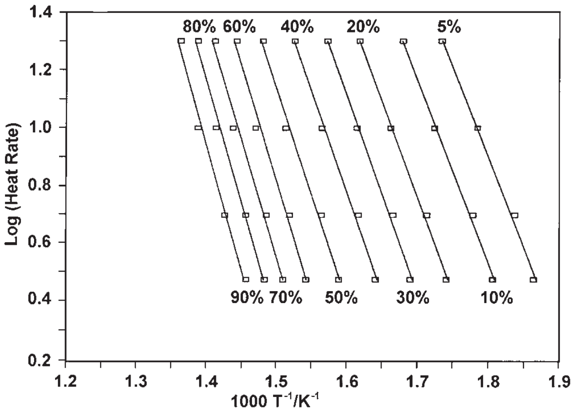


Fig. 9 Plot of logarithmic heating rate *vs*. temperature

rial (18%), comprises char, pigment and fillers. The element and the chemical groups which lead to char formation in this case are nitrogen in the urethane link and the aromatic ring of the isocyanate which constitute the backbone of PU. The contribution due to individual peak was not taken into consideration. The activation energy of decomposition of PU coating was calculated in the range of 300 to 500°C (where the polymeric coating primarily decomposed), using Flynn and Wall method [10]. The first step for that is to make a plot of percent decomposition at different heating rates. Figure 8 illustrates the shift in temperature for several mass loss values as a function of heating rate. The next step is to make a semilogarithmic plot of heating rate *vs*. reciprocal temperature for selected level of conversion (Fig. 9). The slope of the lines represent the activation energy of decomposition for mass losses from 5 to 90% using the method of Flynn and Wall [10] as follows:

$$E=-R/b[\mathrm{dlog}\beta/\mathrm{d}(1/T)] \tag{5}$$

where E – activation energy (J mol^{-1}), R – gas constant, T – temperature at constant conversion, β – heating rate (°C min^{-1}) and b – a constant and taken as 0.457. Figure 10 shows the plot of activation energy at different percent decomposition of the coating. The activation energy increases monotonically as disruption of chemical bonds takes place. Figure 11 shows the degradative stability of the PU coating under different isothermal conditions. The mass loss data at three different temperatures in nitrogen are shown in the figure. Each line represents the mass remaining in mg as a function of time at various temperatures. To evaluate the kinetics, the rate of mass loss was first calculated. The rate of mass loss initially increases to a maximum value at non zero time at a mass loss of about 10% and then it gradually levels off. This indicates that the decomposition reaction consists of consecutive reactions. From the

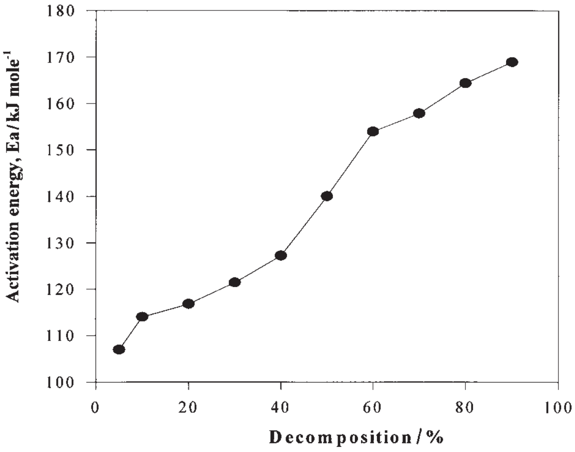


Fig. 10 Activation energy *vs.* % of decomposition

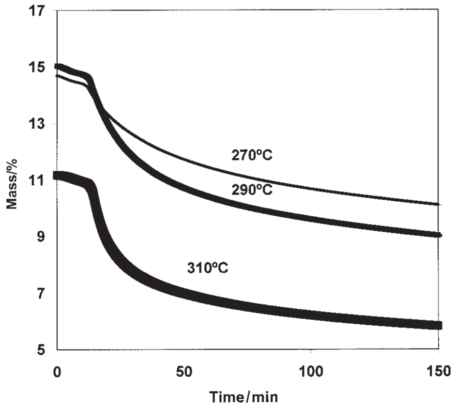


Fig. 11 Isothermal TGA curves at different temperature

isothermal decomposition, the activation energy for the first part of decomposition was calculated and found to be 108 kJ mol^{-1}, which is in good agreement with the activation energy determined by non-isothermal method at 10% decomposition.

Glass transition and elastic modulus

TMA and DMA

As organic coatings are viscoelastic in nature, the T_g, the temperature at which the coating changes from a glassy and hard material to a viscoelastic material is very important to predict the performance of the coating with variation in temperature. Different thermal techniques such as TMA and DMA were used to measure the T_g and elastic modulus of the coating cured at ambient conditions. TMA measures geometric changes in samples as a function of time, temperature, or force. It uses a weighted probe, in direct contact with the sample, to record geometric changes. Figure 12 shows dimension change of the coating at room temperature under different loads. The type of probe used determines the mode of operation of the TMA, how stress is applied to the sample, and the amount of that stress. Samples should have a uniform thickness and be flat on both sides to ensure contact with the weighted probe. Elastic modulus was obtained from the slope of the line by plotting the load (F) *vs.* ($p^{3/2}$) according to the equation proposed by Gent [11].

$$E_m=(F/p^{3/2})(9/16r^{1/2}) \tag{8}$$

where p is penetration.

The elastic modulus for PU coating has been found to be 135.5 mN m^{-2}.

Dynamic mechanical analysis senses any change in molecular mobility in the sample as the temperature changes. The time required for this molecular motion to occur is dependent on the frequency of the applied stress. Transition occurs when the molecular time scale corresponds to the experimental time scale. To study both cured and uncured samples in particular the crosslink density, DMA was used, from which many chemical and physical properties such as solvent resistance, hardness, durability of coating could be evaluated. DMA carried out on the films of coating is shown in Fig. 13. Elastic and loss moduli of the uncured and cured films were represented over a range of temperatures. The highest value of E' is observed in the glassy region which is 2414 MPa. As E' is a measure of material's stiffness, therefore, it can be used in the same way as in TMA to evaluate the crosslink density or degree of cure. The difference in storage modulus before and after glass transition ($\Delta E'$) is regarded as a measure of degree of crosslink density. A smaller $\Delta E'$ is generally associated with higher crosslink density [12, 13]. The maximum tanδ value was chosen as the glass transition temperature (T_g). Both storage and loss properties are useful in such evaluation. An incompletely cured material will exhibit a recovery in the storage modulus as residual cure takes place during heating in the DMA. The T_g after curing at different temperatures was thus compared to ensure appropriate curing. It was interesting to note that if the sample is not properly cured, the T_g value is lower and an initial increase in elastic modulus is observed with temperature as shown in Fig. 13.

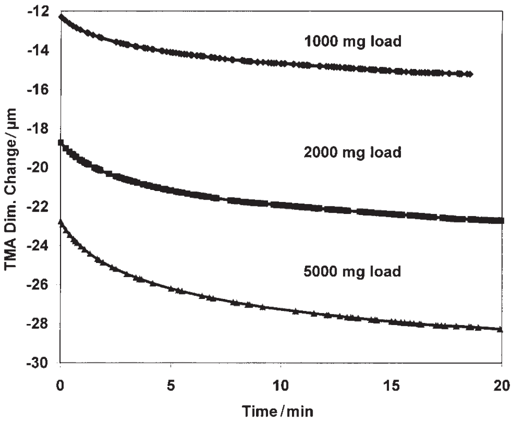


Fig. 12 Dimension change of PU under different load by TMA

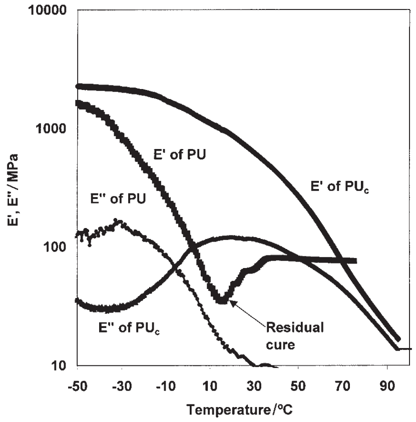


Fig. 13 Effect of curing on the relative storage and loss moduli

As coating becomes more crosslinked, the free volume of the material decreases and T_g increases. Thus a partially cured system shows a T_g of 9°C, while on curing T_g value is 30°C (from tanδ values). The coating also exhibits a very broad and high E'' (Fig. 13) over a broad temperature range. High E'' represents greater mobility of the chains associated with dissipation of energy when subjected to deformation. In addition, it suggests the coating's ability to absorb energy associated with impact.

Conclusions

The use of different thermal techniques provides insight into physical and chemical factors affecting the curing process characteristics, and degree of cure of the coating which determine its performance. The curing reactions from various techniques such as PDSC, DMA and rheometry show the temperature dependency of activation energy and hence rate of curing. In situ, ATR-FTIR shows the formation of urethane linkage over time. Decomposition of PU coating is bimodal. The activation energies of the initial step for both iso and non iso TGA (10% decomposition) are very consistent. DMA shows difference in T_g and E' due to the different state of cure. Also the coating exhibits a high and broad E'', indicating its ability to absorb impact energy.

* * *

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References

1 Z. W. Wicks, Jr., F. N. Jones, S. P. Pappas and N. Y. Wiley, Organic Coating: Science and Technology, Vol. 1, 1992.
2 S. Paul, (Ed.) Surface Coating: Science and Technology, John Wiley, New York 1996.
3 C. M. Neag, ANTEC, SPE, 1191, 1989.
4 T. C. Patton, in Polyurethane Technology ed. P. F. Bruins, John Wiley & Sons, New York 1969.
5 D. M. Crawford, Proc. of the 26th NATA Conference, Cleveland, Ohio Sept. 13-15, 1998 p. 622.
6 T. Hatakeyama and F. X. Quinn, Thermal Analysis Fundamentals and Applications to Polymer Science, John Wiley & Sons, 1994.
7 E. A. Turi, (Ed.) Thermal Characterization of Polymeric Materials, Academic Press, New York 1997.
8 G. Woods, The ICI Polyurethane Book, John Wiley, New York 1990.
9 G. Ortel, Polyurethanes Handbook, Hanser, New York 1985.
10 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
11 A. N. Gent, Trans. Inst. Rubber Ind., 34 (1958) 48.
12 D. J. Skrovanek and C. K. Schoff, Prog. Org. Coat., 16 (1988) 135.
13 L. W. Hill, J. Coat. Tech., 64 (1992) 29.