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

THERMAL ANALYSIS CHARACTERIZATION OF A COMMERCIAL THERMOPLASTIC/THERMOSET ADHESIVE

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Abstract

DSC, TGA and DMA thermal analysis techniques are used to characterize a complex adhesive blend. The chemical and thermomechanical property development shown to follow a two-stage process. Beneficial synergy between these analysis tools is demonstrated in this study.

Keywords: adhesive, composition analysis, curing kinetics, DMA, DSC, TGA, thermal cure, thermoplastic/thermoset blend

Introduction

A complex adhesive blend was characterized using thermal analysis techniques to investigate the cure kinetics and the development of mechanical properties over several decades of time. The adhesive is part of a reinforced tape system used in industrial applications. The studies indicated that the blend was comprised of two phases – an elastomeric, acrylonitrile-butadiene phase and a glassy, thermosetting, phenolic phase. The material followed a two-stage curing process – a first stage, referred to as Regime I, where the storage modulus increased rapidly and a diffusion controlled second stage, referred to as Regime II, where the development of modulus was considerably slower. The results demonstrate the power of various thermal analysis tools for increasing understanding of industrial polymers and controlling compositional variability in applications.

Materials

The material is a heat activated, dry film adhesive consisting of the following ingredients: a phenol-formaldehyde polymer, an acrylonitrile-butadiene polymer, zinc oxide and N,N'-di(2-naphthyl)-*p*-phenylene diamine. The phenolic polymer represents the

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thermoset and the acrylonitrile-butadiene copolymer represents the thermoplastic/elastomeric component of this commercial blend. The zinc oxide and the diamine antioxidant are included as additives. The elastomeric components are important to the flow characteristics of the tape when used and the thermosetting resin provides the application with integrity and thermo-mechanical stability.

Phenolics are resinous materials produced by the condensation of phenol, or a mixture of phenols, with an aldehyde such as formaldehyde. Under appropriate conditions these condensation products form resoles or Novolacs which when reacted with a hardener, produce a cross-linked network. Typically, this type of resin begins to react at an appreciable rate when heated above its glass transition temperature (T_g). The reaction primarily occurs via methylene bridging with the simultaneous liberation of volatiles and heat. A number of thermal characterization methods are available for monitoring the progress of such a reaction. The liberation of volatiles can be tracked quantitatively by ThermoGravimetric Analysis (TGA) and exothermic heat of reaction can be tracked by using Differential Scanning Calorimetry (DSC), provided there are no complications from the loss of volatiles [1]. In addition, Dynamic Mechanical Analysis (DMA) provides a means for characterizing the cure reaction and generates information about the linear viscoelastic properties (i.e., independent of the magnitude of stress or strain amplitude) of the materials, once cured.

Characterization methods

The glass transition temperatures for the uncured and cured samples (5 to 10 mg sample size) were measured using both a Perkin Elmer DSC 7 Differential Scanning Calorimeter and a Pyris unit. While the former device uses nitrogen as a purge gas and has a lower operating limit of –60°C, the Pyris unit is purged with helium and has a low temperature limit of –170°C. A heating rate of 15°C min^{-1} was used for all the scans. The glass transition temperature, T_g, was recorded at $\frac{1}{2}\Delta C_p$ and the width of the transition, ΔT_g, was determined from a difference of the extrapolated beginning and end of the transition [2]. The heat of reaction, ΔH_r, could not be accurately measured due to a loss of condensation products from the curing reaction even when the sample was hermetically sealed in stainless steel pans.

Dynamic thermogravimetric analysis was performed on the Perkin Elmer TGA 7 Thermogravimetric Analyzer and used to evaluate the extent of cure and the thermal stability of the materials. All the dynamic scans were recorded between 23 and 700°C at a heating rate of 15°C min^{-1} and the mass loss was measured as a function of temperature. In addition, isothermal TGA curing studies were carried out in a dry nitrogen atmosphere at 100, 125, 150, 175, 200 and 225°C. In each case, a 5 mg sample of the adhesive was held at 23°C for 5 min and heated at an appropriate rate to arrive at the selected cure temperature in exactly 3 min. So, for instance, to reach 125°C in 3 min, a heating rate of 33.33°C min^{-1} was utilized.

The Dynamic Mechanical behavior was observed on the Rheometric Scientific RSA-II and RDS-II at a frequency of 1 rad s^{-1} and a heating rate of 2°C min^{-1}. In addition to the storage modulus (E') and the loss modulus (E''), tanδ curves were obtained for all samples. The glass transition temperature was measured as the maximum in the tanδ curve. Isothermal measurements were performed in tension at 100, 125, 150, 175, 200, 225 and 250°C and again, E', E'' and tanδ were monitored.

Observation and results

A DSC scan of the uncured, 'as received' material from –40 to 100°C shows two glass transition temperatures at 7 and 75°C (Fig. 1, scan #1). The two T_gs are indicative of the presence of two amorphous phases in the adhesive material. The lower T_g, we believe, corresponds to the rubbery or elastomeric acrylonitrile-butadiene phase and the higher T_g is associated with the glassy, thermosetting phenolic resin. On the same figure, scans #2 and #3 correspond to commercial acrylonitrile-butadiene (ACN/BD) copolymers containing 41/59 and 51/49 mass percents of ACN and BD with T_gs of –14 and –2°C respectively. Since the latter polymer's T_g is within 10 degrees of the glass transition temperature of the copolymer phase of the adhesive resin, it indicates that the mass ratio of the ACN to BD in the adhesive mixture is roughly 50/50. A more accurate estimate of the ratio cannot be made in this case due to partial mixing of the phenolic resin with the ACN-BD copolymer. The width of the glass transition (ΔT_g) for the ACN/BD copolymer in the adhesive blend is roughly 16°C, while that for the two commercial blends is about 7°C. The broadening of the glass transition for the adhesive results from the partial mixing of the phenolic resin with the elastomeric copolymer. Mixing should lead to enhanced interfacial adhesion and mechanical properties within the domains of the poly-blend with efficient transfer of stress across the domain boundaries [3]. In addition, from the ratio of ΔC_p at T_g for the

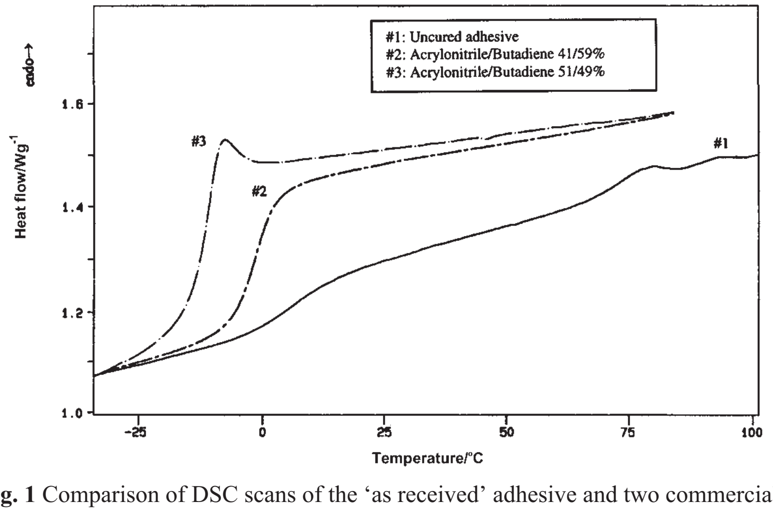

Fig. 1 Comparison of DSC scans of the 'as received' adhesive and two commercial copolymer blends

elastomeric component of the blend and copolymer, ACN/BD (51/49), which have values of 0.30 and 0.45 J g^{-1} $°C^{-1}$, respectively, a fraction of 0.67 ACN/BD copolymer is estimated to be present in this blend.

Figure 2 (solid line #1) is a scan of the 'as received' sample to above the glass transition temperature of the uncured phenolic phase, i.e. 75°C. This causes an exothermic reaction to be initiated at 100°C with a maximum rate of heat evolution near 150°C. The first scan was intentionally terminated at 170°C because the excessive out-gassing caused noise in the DSC output. By scanning the same material repeatedly and taking the sample to higher temperatures each time, the noise in the output was considerably lowered. The fourth scan (#4) shows a large exotherm with about 45 J g^{-1} of heat liberated, as the thermoset reaches a maximum in the reaction rate near 235°C. The T_g of 75°C observed clearly in scan #1, gets broader and more difficult to see in the subsequent scans indicating additional cure in the sample with each scan.

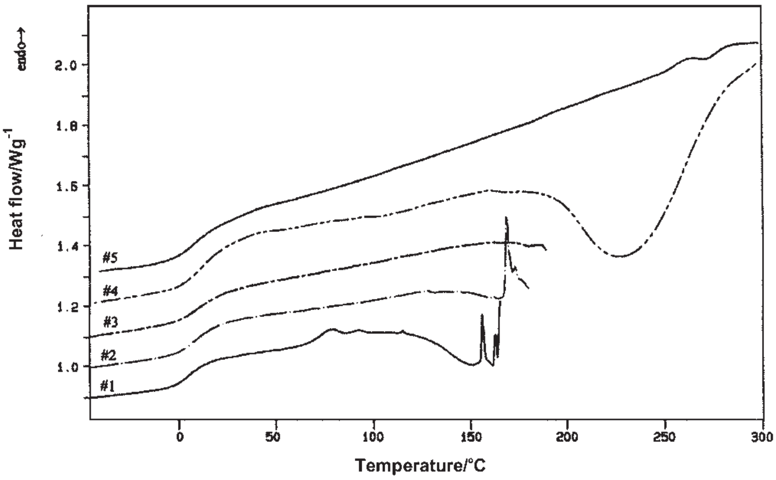

Fig. 2 Successive curing of adhesive blend by DSC

The T_g of the cured thermoset was obtained from a sample of the adhesive aged for an hour at 220°C and then scanned from –20 to 300°C at 15°C min^{-1} (Fig. 3). The onset of the T_g for the cured phenolic is observed at 150°C, with a mid-point ($1/2\Delta C_p$) near 235 °C and an end-point near 260 °C. During each run, with the advance of the sample's cure state, the placement and magnitude of the lower T_g, associated with the thermoplastic phase, is essentially constant. This indicates that the cured thermoset has not restricted the molecular motions of the rubbery phase of the adhesive.

The thermal stability, degradation and extent of cure were also characterized by TGA analysis. Here the mass loss for the 'as received' but pre-dried sample was monitored as a function of time from 23 to 300°C at a heating rate of 15°C min^{-1} (dotted line, Fig. 4). At 300°C, approximately 10% mass loss was observed, probably corresponding to the evolution of low molecular mass reaction products resulting from the

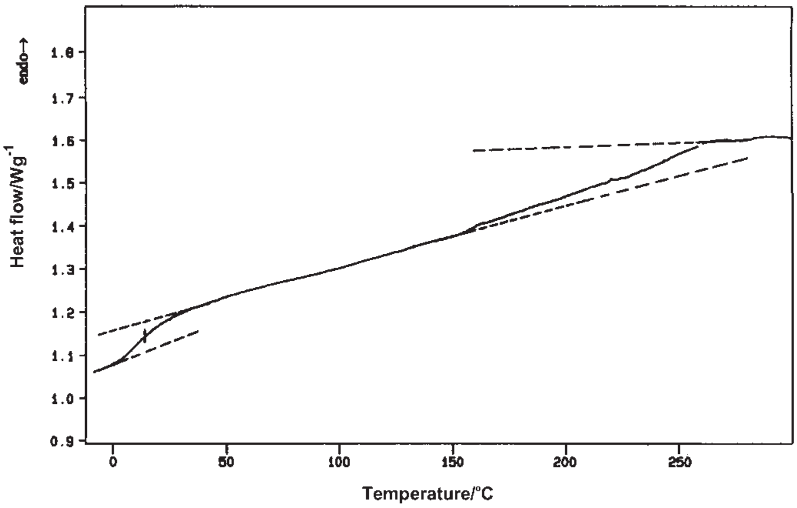

Fig. 3 DSC scan of the adhesive cured and aged at 220°C for one hour

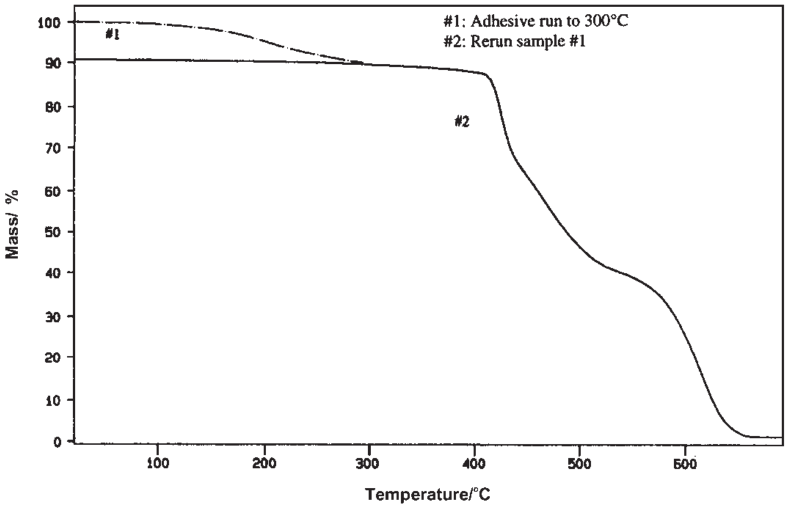

Fig. 4 TGA profiles of 'as received' but pre-dried adhesive sample

cure of the phenolic resin. Re-scanning the same sample from 23 to 700°C showed no sign of mass loss until a temperature of 400°C was reached (solid line, Fig. 4). Above this temperature, degradation of the polymer began and low molecular mass products resulted. The derivative mass loss curve of the re-run sample is shown in Fig. 5 (dashed broken line). Three maxima at 420, 470 and 620°C are observed and appear to be associated with the degradation of the three major components in the adhesive blend; namely, butadiene, acrylonitrile and phenolic respectively.

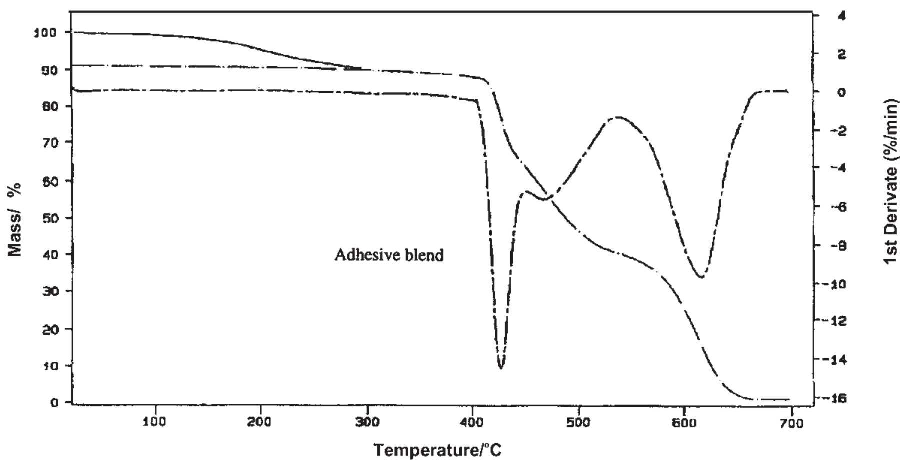

Fig. 5 Derivative mass loss curve for adhesive blend

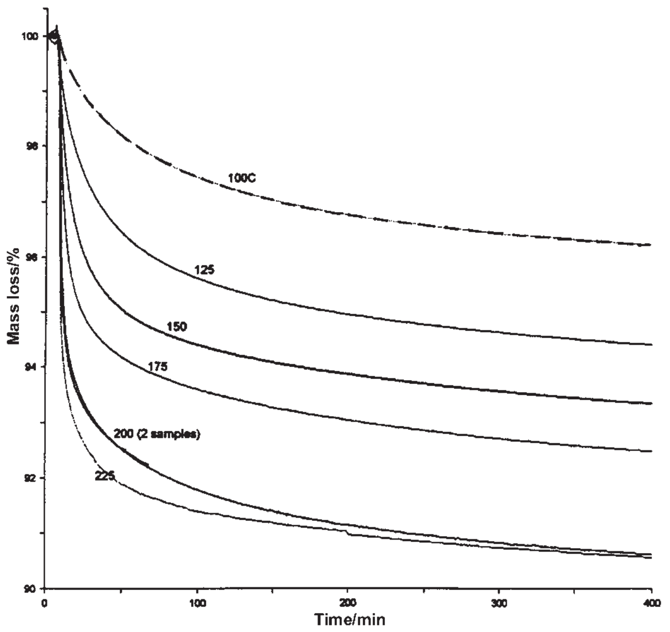

Fig. 6 TGA mass loss monitored as a function of time at different temperatures

It is possible to use TGA analysis to perform compositional analysis on certain copolymers, provided that the different segments in the copolymer chain have significantly different thermal stabilities [4]. In this case, IR analysis of the evolved gases from the TGA experiment indicate that some breakdown of the phenolic resin is occurring during the degradation of the elastomeric copolymer in the temperature range of 370 to 500°C, and hence, the TGA analysis cannot be used to directly estimate the level of the individual components in this unknown thermoplastic/thermosetting blend. Nevertheless, the TGA fingerprint should be useful as a quality control check for the consistency of the incoming material.

The residual ash (at 700°C) is 2% by mass and probably corresponds to the zinc oxide additive referred to in the product data sheet (Fig. 5). Thus, if the blend contains 67 mass% thermoplastic copolymer as shown by the DSC phase transition data and 2 mass% zinc oxide from TGA results, the remainder of the unknown composition, the phenolic resin, should equal 31 mass% of the blend.

For several thermosets including phenolics, the evolution of volatiles or condensation products formed during cure can be used as a measure of the degree of conversion. Care must be taken to account for the mass loss associated with contaminants such as absorbed water. If the 10% mass loss of low molecular mass volatiles from the dried film of adhesive represents only the condensation products of the curing phenolic phase, the extent of reaction (χ) equals

$$\chi = \text{mass loss}/10$$

where the mass loss is the mass percent of volatiles resulting from the heating of the material to 300°C.

Figure 6 illustrates the mass loss associated with reacting the adhesive samples at temperatures of 100, 125, 150, 175, 200 and 225°C respectively. In each of the experiments, the sample was initially held in nitrogen at 23°C for 5 min and then heated for 3 min until the temperature of interest was reached. At each temperature, the reaction appears to follow two stages. In the early stages of curing, the reaction temperature is above the material's glass transition temperature and the reaction proceeds at a rapid rate (i.e. mass decreases rapidly). In the later stages when the T_g also increases and exceeds the reaction temperature, the reaction rate becomes diffusion controlled.

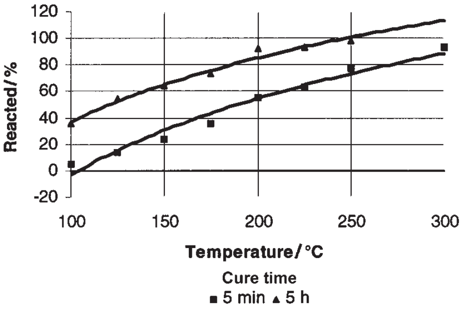

Fig. 7 Percentage of the thermoset reacted at various temperatures as determined by TGA analysis

Then, the molecular motions are restricted and the reaction slows down (i.e. a plateau is observed in the mass loss curve) [5–8].

Using the above equation and the data in Fig. 6, the extent of cure of the phenolic phase at 100, 125, 150, 175, 200, 225 and 250°C after 5 min is calculated to be 5, 14, 24, 36, 55, 63 and 77% respectively. The reaction at the above mentioned temperatures was continued for a period of 5 h and the total percentage cure was calculated. Figure 7 illustrates the total percent cure of the thermoset as a function of time at the different temperatures after 5 min and 5 h of exposure. Obviously, the rapid development of the phenolic network is facilitated at higher temperatures and/or longer times. Higher temperatures can however, lead to discoloration and degradation of the elastomeric component in the blend. For optimum results, the maximum bond strength of the material should be correlated with temperature responses to achieve the most reaction without compromising on chemical stability.

In addition to DSC and TGA analyses, Dynamic Mechanical measurements were performed to study the chemical conversion and the development of the T_g of the partially cured and fully cured materials. The T_g is typically measured as a maximum value in the loss modulus, loss compliance or tanδ curves in a temperature scan. The DMA scans were performed on the RSA-II and the energy dissipation was measured by the peak in the tanδ curve. The adhesive sample was ramped up from –150 to 350°C at 2°C min^{-1} and at a frequency of 1 rad s^{-1}. Figures 8 and 9 illustrate the variation of storage modulus, loss modulus and tanδ over curing time as the reaction proceeds from an uncured to a fully cured state. The first drop in the storage modulus

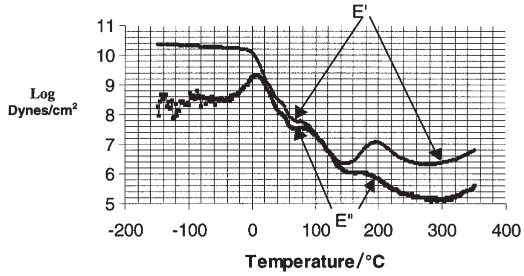

Fig. 8 DMA scan of the uncured adhesive blend from –150 to 350°C (1 rad s^{-1})

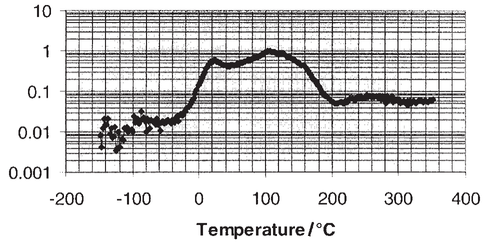

Fig. 9 DMA tanδ scan of the uncured adhesive blend from –150 to 350°C (1 rad s^{-1})

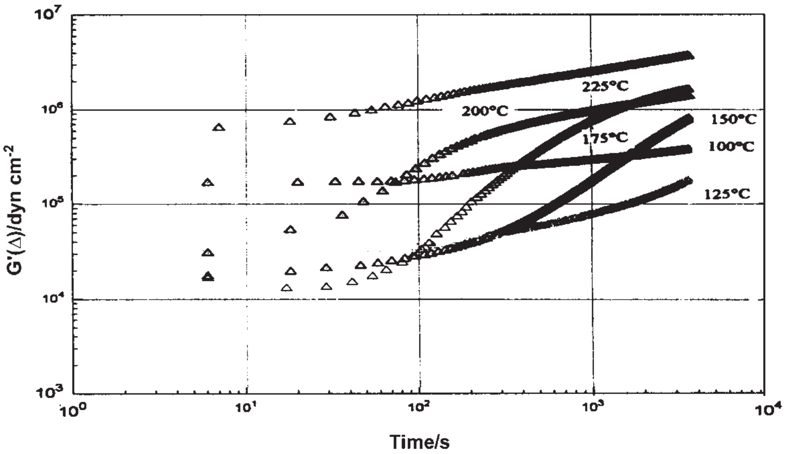

Fig. 10 DMA isochrons in the 'cure window' for adhesive blend

occurs below room temperature and corresponds to the glass transition temperature of the elastomeric component i.e. the ACN/BD blend. The T_g of the uncured thermosetting component is noticeable at ~75°C as is the cure exotherm between 150 and 250°C. Beyond 250°C, the storage modulus is observed to further increase. Isochrons were performed in the 'cure window' (at 100, 125, 150, 175, 200 and 225 °C) to better characterize the cure behavior (Fig. 10). These measurements were done on the RDS-II using the parallel plate geometry (sample: 160 μm thick, 25 mm diameter). As shown in Fig. 10, a two stage development of the modulus of the thermosetting phase, similar to the kinetic curing scheme outlined in Fig. 6 is observed. That is, there is a transition from Regime I, where modulus increases rapidly to Regime II, characterized by a slower modulus development. This transition occurs within a few minutes at higher temperatures and takes longer at lower temperatures. Surprisingly, the change in modulus at 100°C does not seem to follow this two-stage regime process, in that the modulus at the start of the scan is higher than most initial values. Analysis of the extent of cure at 100°C by TGA indicates that a small amount (about 5%) of the reaction takes place even when the reaction temperature is below the T_g and therefore the modulus of the material remains relatively high. At 125°C however, the reaction temperature exceeds the T_g for a short time and the modulus is significantly lowered until the material enters the second stage of curing.

The T_g and equilibrium modulus can be used as a measure of the extent of cure. In the system of interest, the equilibrium modulus is well below the initial glassy modulus. Since the T_g of the fully cured network lies within the cure window, vitrification occurs as the material cures and the T_g catches up with the cure temperature. A higher modulus can be achieved if the material is exposed to either higher temperatures or held at a given temperature for a longer time. At this stage, degradation processes will start to compete with the chemical crosslinking, complicating the overall cure process. Time temperature superposition techniques may be applied to materials to predict the behavior of the material over several decades of time [9, 10]. The

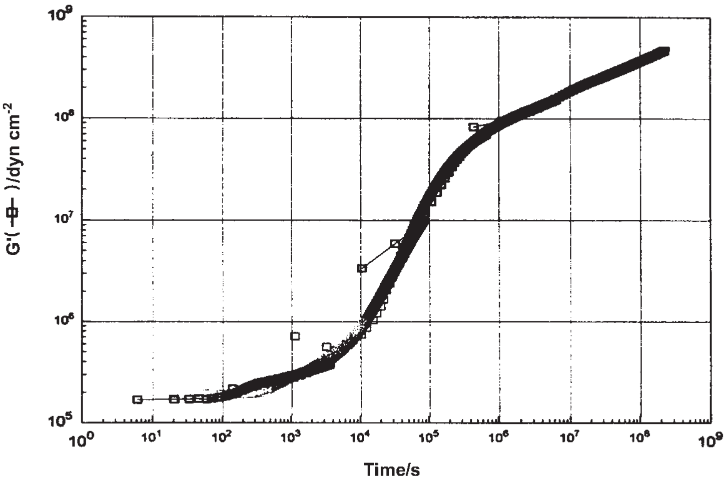

Fig. 11 G' master curve for adhesive blend obtained by time-temperature superposition

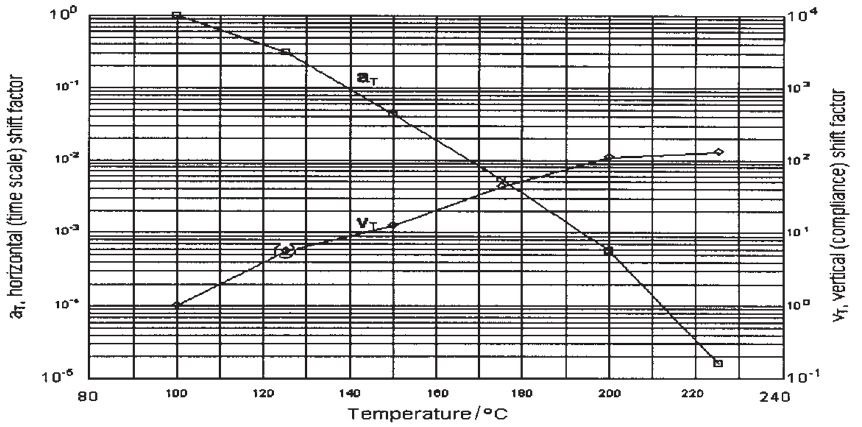

Fig. 12 Horizontal and vertical shift factors

method permits the characterization of viscoelastic relaxation processes and the extrapolation of time-temperature mechanical data to regions beyond the scope of the measurement method. Thus mechanical measurements can be made in reasonable time scales and utilized to address material/component properties over their respective lifetimes. The superposition principle is largely based on the observation that time and temperature effects in polymers are essentially equivalent. Increasing the temperatures is equivalent to shifting the same event to shorter times or lower frequency and increasing the frequency is equivalent to shifting the same event to lower temperatures.

This leads to the concept of shift factors that ratio the corresponding times for which the same viscoelastic behavior occurs at different temperatures,

$$\text{i.e. } a_T = t_{T1}/t_{T2} = f_{T2}/f_{T1}$$

The WLF equation (developed by Williams, Landel and Ferry) gives a good description of the shift-factor-temperature relationship above the T_g of the material [11]. In the sub-T_g region, the shift factors are better described by the Arrhenius equation that treats the shift factors as transition states with a characteristic activation energy. Typically, the technique is applied to polymer systems that are not changing chemically with time at constant temperature. Time-temperature superposition techniques can also be applied to polymer systems during the curing process to better understand the cure kinetics and establish a connection with mechanical property development.

Figure 10 represents the storage modulus plotted *vs.* time at six equally spaced temperatures, namely 100, 125, 150, 175, 200 and 225°C. Time temperature superposition was performed on the isochrons to generate the cure master curve for the modulus shown in Fig. 11 using the curve obtained at 100°C as the reference. Figure 12, is a plot of the corresponding shift factors, a_T and v_T, *vs.* temperature. From the master curve it is clear that it would take 12 days at 100°C to enter Regime II of the curing process (10^6 s, Fig. 11). At 225°C however, Regime II would be reached in 10 s (calculated using $a_T=10^{-5}$). Here the vertical shift is essentially a compliance and accounts for the material softening with increasing temperature. Thus using the master curves and the corresponding shift factors, we can not only predict the thermo-mechanical cure behavior for processing times and temperatures considered practical in the manufacturing process, but also specify the degree of control required over these parameters during manufacturing.

Conclusions

Thermal studies of the commercial adhesive blend indicate that it is composed of two amorphous phases. One is a thermoplastic elastomeric copolymer of acrylonitrile and butadiene with a T_g below room temperature (7°C) and the second is a phenolic thermosetting resin. From DSC phase transition studies, the composition of the blend is 67 and 31 mass% in the copolymer and the phenolic resin, respectively. The thermoplastic copolymer in this blend contains approximately a 50/50 mass ratio of acrylonitrile and butadiene. The phenolic component can be reacted readily at temperatures above its T_g and when fully cured has a T_g of 235°C. The kinetics of the conversion of the thermosetting portion of the dry adhesive can be monitored by TGA by measuring the evolution of the resin's condensation products. Dynamic mechanical measurements and time-temperature superposition can be utilized to describe the development of mechanical properties (e.g. elastic modulus) of the material over several decades of time.

The results of this thermo-mechanical characterization study can be utilized as a quality measure to ensure that batches of the adhesive blend have the same composition and cure characteristics. Lastly, the use of this material may be limited at temperatures below the T_g of the thermoplastic phase (i.e. below room temperature), where the material will become very stiff. Improvements in the low temperature performance could be made by increasing the ratio of BD to ACN components in the elastomeric portion of the blend.

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