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Rheological and Thermal Characterization of Polymer Coatings: A Case Study

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This article addresses the value of collecting mechanical and thermal property data for better understanding the development of coating properties. As a case study, the rheological and thermal characterization data of two solventborne systems (a polyamide-cured epoxy and a moisture-cured RTV silicone) and a 100% solids system (polyetheramine-cured epoxy) are discussed along with the experimental considerations when conducting these types of studies. For the two solventborne systems, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to characterize the liquid-to-solid transformation of these functional coatings. In particular, for the polyamide-cured epoxy, the effects of solvent addition and cure temperature (ambient vs heat-cured) on the resulting properties were investigated. For the 100% solids polyetheramine-cured epoxies, an in situ DMA immersion test for measuring the solvent resistance of coatings is presented. For these materials, lower crosslink density formulations exhibited more dramatic decreases in modulus with solvent uptake.

INTRODUCTION

Polymer coatings are applied to a substrate to impart or improve a particular property or functionality. Among others, the properties that can be enhanced through the use of coatings are aesthetic, mechanical, protective, anticorrosive,[1] conductive,[2] and biomedical[3] in nature. Polymer-based dispersions or solutions use water or organic solvent(s) as the vehicle for applying the coating to the substrate, where the use of solvent often helps improve the film formation process.

For these coatings to be successful, transformation of the initially liquid material to a solid, film-formed state of given properties is essential. Although extensive analytical tests or techniques are available for characterizing the liquid coating and the final solid film, less characterization effort is devoted to measuring the properties during the coating drying or curing process. The reason for this may be that film formation involves a change of physical state, loss of material, and property changes that vary by many orders of magnitude so

that finding an experimental apparatus and geometry can be challenging. Despite the difficulties, characterization of the transformation from the liquid to solid state is critical to understanding the resulting coating properties. As a result, these data are necessary to properly specify a material for a given application, as well as for designing next-generation coatings that address the limitations of current materials.

Various techniques are available for measuring the properties of polymer coatings. Among others, these include thermal methods[4,5] such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA), mechanical methods[6,7] such as DMA and nanoindentation,[8] as well as impedance spectroscopy.[9,10] Because these techniques are complementary, mechanical methods are often coupled with thermal methods for characterizing coatings.[11-15]

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One of the challenges associated with performing a more complete characterization of the mechanical properties of coatings is the ability to obtain free-standing pieces. In the absence of a free-standing polymer film, experimental conditions that ensure that the results are not dominated by the typically stiffer and more massive substrate must be employed. Despite the challenge of a substrate, researchers have been able to characterize the mechanical properties of the polymer coating without removing the substrate.[8,16-18] Similar considerations apply when trying to use TMA to characterize coatings on substrates. To collect more complete data, efforts were made in this work to produce free-standing coating films.

As a case study, two solventborne systems were chosen: a polyamide-cured epoxy and a moisture-cured room temperature vulcanizing (RTV) silicone. For the epoxy system, a diglycidyl ether of bisphenol A (DGEBA)-type resin was mixed with a high imidazoline content polyamide, and xylene as a solvent. A one-part, moisture-cured RTV silicone dispersion that can be used as a conformal coating was used for the silicone system. In addition, a 100% solids system comprised of a DGEBA-type epoxy resin cured with a blend of polyetheramines was examined.

These two solvent-based systems were chosen as representative examples of polymer coatings; commercial formulations may be more complicated. The use of these three systems in this work is for illustrative purposes only.

EXPERIMENTAL

Three systems were chosen to demonstrate the utility of using rheological and thermal techniques to characterize coatings. In particular, DMA and DSC were employed to characterize the rheological and thermal properties, respectively.

Briefly, DMA uses a sinusoidal deformation to measure the rheological properties of a material, including the storage modulus (E′ or G′), loss modulus (E″ or G″), and tan(δ).[19] Tan(δ), which is equal to E″/E′ or G″/G′, is a measure of the degree of viscoelasticity of a material, or, more simply, the balance between liquid-like and solid-like and properties. Rheological properties are commonly determined as a function of temperature and frequency; both of these variables are illustrated in this work. For the rheological testing of coatings, free-standing films are preferred, since the results are not influenced by the mechanical properties of the substrate and the characterization can be more definitive. It is recognized that, for some coatings systems, obtaining a free-standing film may not be possible. As will be discussed below, atypical substrates were used in this work to afford free-standing films. While using the actual substrates associated with a given application has merit, the approach used herein enables a greater level of understanding of the coating system.

Specifically, an RSA G2 rheometer (TA Instruments) was used to measure the tensile dynamic mechanical properties for both coating systems as a function of cure time. This rheometer was also used to measure the mechanical properties of polyetheramine-cured epoxies during immersion in water as a demonstration of an in situ method for examining the solvent resistance of a coating.

DSC measures the heat flow into or out of a sample relative to a reference standard and enables one to measure properties such as the glass transition temperature (T_g), heat of reaction, and degree of cure for thermosetting systems. DSC must be used with care when applied to water- or solventborne coatings as evaporation of residual solvent can often dominate the resulting thermal signal. For semi-crystalline thermoplastic polymers, DSC is useful for examining the degree of crystallinity, as well as the breadth of the crystal melting and crystallization profiles. Two heating scans were used in this study; the first scan measures the properties of the material in its current state, while the second scan determines the properties after nearly complete cure. For this work, a Q200 DSC (TA Instruments) was used. Given the relatively small sample size used for DSC (20 mg), representative sampling is important.

Initial experiments using TGA to examine solvent loss as a function of time for the polyamide/epoxy/xylene formulations were largely unsuccessful as the expected monotonic trend in loss of solvent was not observed. The relatively thick films used made it difficult to obtain representative coating specimens for testing. Since a gradient in solvent concentration through the thickness of the coating will exist until all of the solvent is lost, taking samples for TGA testing only from the bulk or the surface will result in data that are not characteristic of the coating.

Polyamide/Epoxy Formulations

A stoichiometric mixture of a DGEBA-type epoxy resin and a polyamide curative was prepared and served as a 100% solids control. In addition, a stoichiometric formulation of the same epoxy resin and polyamide curative was prepared with 20% by weight xylene (based on the total resin and curatives weights) to illustrate the impact of solvent on mechanical properties. For these epoxy-based formulations, about 1/32-in. thick specimens were cast into silicone rubber molds for subsequent rheological and thermal testing. Relatively thick coatings were used to facilitate sample handling and lengthen the time required for solvent removal. Rheological and thermal properties were measured after 2, 6, and 21 days of cure at ambient temperature and humidity. Because the results of initial DSC testing performed on the samples with xylene were dominated by solvent evaporation, subsequent DSC data were not collected on this solventborne system.

Heat-cured specimens of the 100% solids and xylene-modified formulations were also prepared to compare the properties of the coatings cured at ambient temperature with those ultimately attainable using an elevated temperature cure. Heat-curing consisted of one hour at 120°C in a forced air oven after 21 days of cure at ambient temperature.

The tensile dynamic mechanical properties of the ambient- and heat-cured polyamide/epoxy coatings (both with and without xylene) were measured as a function of temperature over the –50 to 120°C range using a 5°C/min ramp. This relatively high ramp rate was chosen to facilitate capturing the true mechanical properties of the coating and minimizing additional sample cure within the rheometer. Data were using a 6.28 rad/s deformation frequency.

Moisture-Cured RTV Silicone Formulation

An as-received RTV silicone dispersion sample was cast 20 mils wet on a silicone rubber substrate (to facilitate subsequent removal of the coating for mechanical testing). Although it is recognized that some of the solvent in the dispersion may diffuse into the silicone rubber substrate during cure thereby altering the cure rate, this shortcoming was deemed not to be particularly relevant for the purpose of this work. Immediately after casting, the coatings were placed in an environmental chamber held at ambient temperature and 30% relative humidity (RH). Free-standing films were carefully peeled from the substrate and the tensile dynamic mechanical properties of the coatings were measured after 1 hr, 24 hr, and 7 days of cure at ambient temperature and 30% RH. For improved statistics, two specimens were measured for each test and each time point.

For each time point, rheological properties were obtained in tension as a function of frequency over the 1 to 100 rad/s range. To minimize any further evaporation of solvent, testing was conducted at ambient temperature and did not use the RSA G2's environmental chamber (which uses a flow of dry N_2 to control temperature).

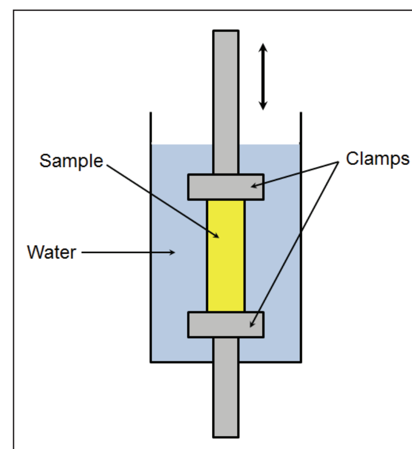
Polyetheramine/Epoxy Blends

Because polyetheramine (PEA) curatives are available in a wide range of functionality and molecular weights, they offer the opportunity to make networks of defined structure. A series of PEA-based formulations was prepared with a DGEBA-type epoxy to demonstrate the use of an in situ rheological technique to examine the solvent resistance of coatings, which is especially important in the potential use of coatings in protective or secondary container-type applications.

A relatively low molecular weight diamine polyetheramine (PEA Low) and a relatively high molecular weight diamine polyetheramine (PEA High) were selected as curatives. Specifically, 60/40, 70/30, and 80/20 blends (by weight) of PEA Low/PEA High curatives were examined. For each blend, a stoichiometric mixture was prepared with a DGEBA-type epoxy resin, cast into ~10 mil-thick films, and heat-cured for 3 hr at 150°C in a forced air oven. The choice of these blends was made to produce materials that illustrate the impact of solvent uptake on a convenient experimental time scale.

In addition to measuring the tensile dynamic mechanical properties of these three formulations as a function of temperature (similar to that performed for the polyamide/epoxy materials), the rheological properties of these three materials were measured in tension as a function of immersion time (3 hr) in water at ambient temperature using the immersion fixture of the RSA G2. A schematic of the immersion apparatus is shown in *Figure 1*. Basically, this apparatus consists of a thin-film fixture housed inside a stainless steel cylinder enabling one to submerse a polymer in a fluid of interest (water for these experiments) and collect data as a function of time and/or temperature. This apparatus avoids the difficulties and limitations associated with the more traditional approach of collecting solvent resistance data by avoiding having to remove, handle, and load samples taken from a benchtop vial or vessel containing the polymer and fluid of interest. While water was chosen for these experiments, other fluids of interest (e.g., solvents, oils, etc.) can be used with this apparatus. The safety aspects of immersion experiments performed with a nonaqueous fluid should be considered prior to performing these experiments, especially for nonambient test conditions.

FIGURE 1—Schematic of immersion apparatus for RSA G2 rheometer.



For these PEA/epoxy immersion experiments, 10 minutes of data were collected at ambient temperature prior to the addition of water at ambient temperature to serve as a

baseline for the immersion data. Data were collected every 30 sec using a 6.28 rad/s deformation rate.

RESULTS

Polyamide/Epoxy Formulations

Rheological Data

The tensile dynamic mechanical properties of the polyamide/epoxy/20% xylene sample after two days of cure at ambient temperature and humidity are shown in *Figure 2*. The data show a glassy region up to about 0°C, a T_g region from 10 to 50°C, and a rubbery plateau above T_g. The midpoint T_g, as evidenced by the peak in the tan(δ) data, is 36±2°C. The onset T_g, as evidenced by the peak in the tensile loss modulus (E") data is in the 5–20°C range. The increase in the tensile storage modulus (E') with increasing temperature in the rubbery region indicates that additional cure and/or loss of xylene is occurring while the sample is in the rheometer. This increase in E' is not surprising, considering that the sample may not be fully cured and that solvent is likely still present in the sample.

The data in *Figure 2* are qualititatively similar to those for the other polyamide/epoxy samples (either with or without xylene). As a result, and for reasons of brevity, subsequent figures for the polyamide/epoxy samples only focus on the E' data.

An overlay of the E' data as a function of temperature and cure time for the xylene-based samples cured at ambient conditions, together with the data for the heat-cured sample, is shown in *Figure 3*. The midpoint T_g, minimum in E', molecular weight between crosslinks (Mc), and E' at 120°C data for these formulations are summarized in *Table 1*. The following equation was used to calculate Mc[19]:

$$Mc = [3\rho RT]/E'$$

where ρ is the density, R is the universal gas constant, and T is the absolute temperature. For fully cured thermosets, the E' data at T_g + 40°C are often used to calculate Mc. This was not done in this work

FIGURE 2—Tensile dynamic mechanical properties as a function of temperature for the polyamide/epoxy/20% xylene sample after two days of cure at ambient temperature and humidity.

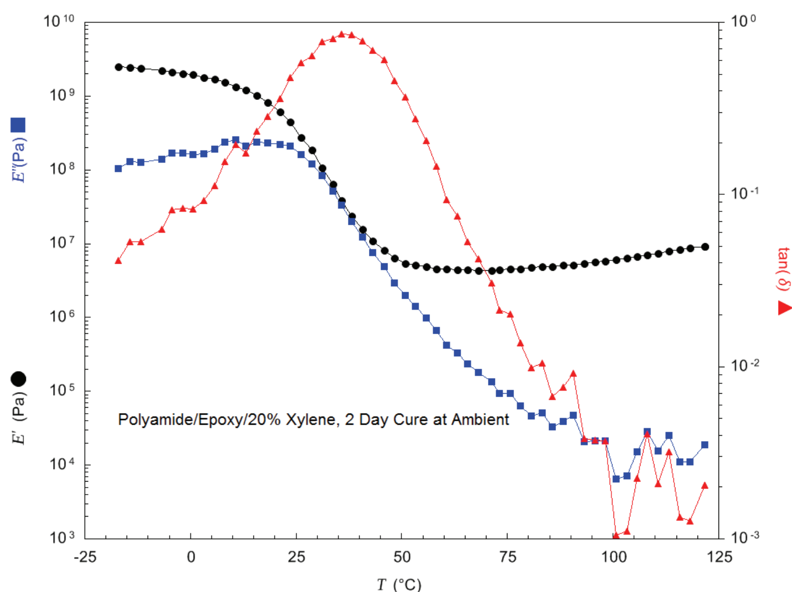


FIGURE 3—Overlay of the tensile storage modulus (E') data as a function of temperature and cure time (at ambient temperature and humidity) for the polyamide/epoxy/20% xylene formulations. Also shown are the data for the heat-cured sample.

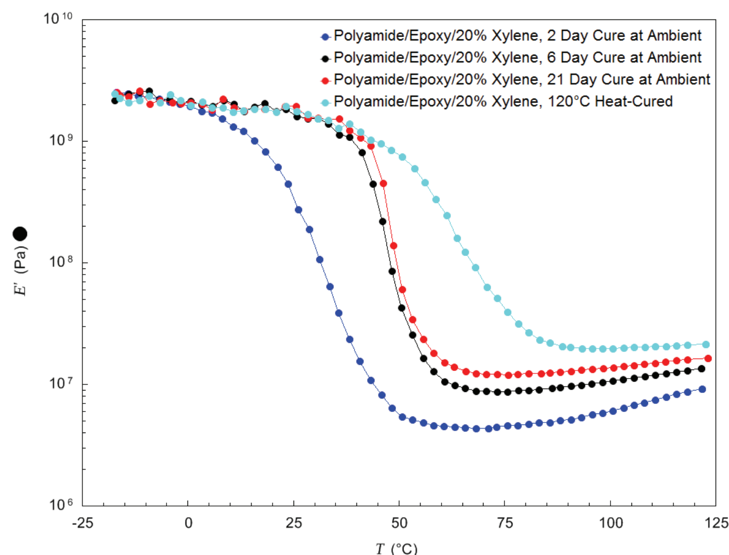


TABLE 1—Summary of the Midpoint T_g, Minimum in E', Mc, E' at 120°C, and Cure Ratio Data for the Polyamide/Epoxy Formulations Prepared with and without Xylene

SAMPLE	CURE CONDITION	MIDPOINT T_g [°C]	MINIMUM E' [Pa]	Mc [g/MOLE]	E' AT 120°C [Pa]	CURE RATIO
POLYAMIDE/EPOXY/20% XYLENE	2 DAYS AT AMBIENT	36	4.33×10^6	1,970	8.90×10^6	2.1
	6 DAYS AT AMBIENT	52	8.74×10^6	990	1.34×10^7	1.5
	21 DAYS AT AMBIENT	53	1.20×10^7	720	1.61×10^7	1.3
	120°C HEAT-CURED	64	1.98×10^7	470	2.14×10^7	1.1
POLYAMIDE/EPOXY	2 DAYS AT AMBIENT	42	2.90×10^6	2,940	9.90×10^6	3.4
	6 DAYS AT AMBIENT	48	4.62×10^6	1,840	1.18×10^7	2.6
	21 DAYS AT AMBIENT	52	6.56×10^6	1,330	1.42×10^7	2.2
	120°C HEAT-CURED	97	2.51×10^7	390	2.51×10^7	1.0

Cure Ratio = E' at 120°C/Minimum in E'

FIGURE 4—Overlay of the tensile storage modulus (E′) data as a function of temperature and cure time (at ambient temperature and humidity) for the polyamide/epoxy formulations. Also shown are the data for the heat-cured sample.

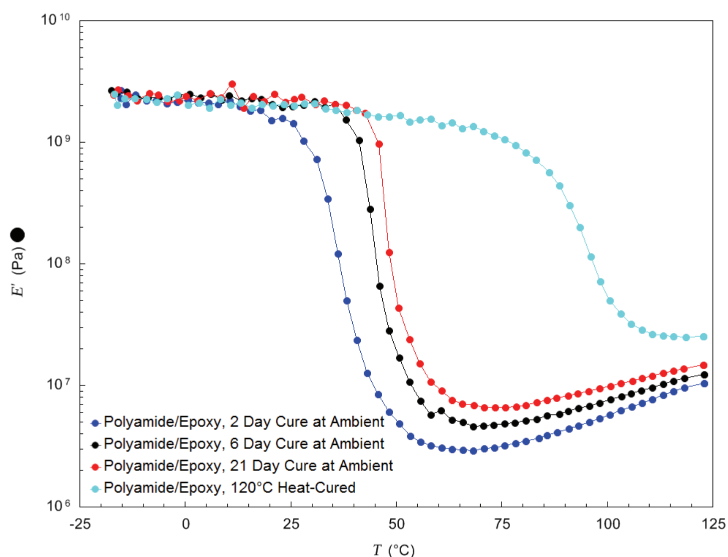
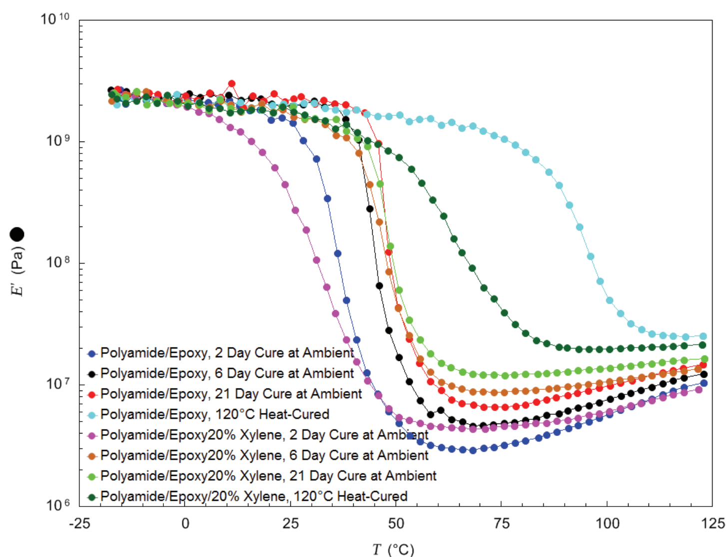


FIGURE 5—Overlay of the tensile storage modulus (E') data as a function of temperature and cure time (at ambient temperature and humidity) for both the polyamide/epoxy and polyamide/epoxy/20% xylene formulations. Also shown are the data for the heat-cured samples.



since E' data at T_g + 40°C would have resulted in additional cure for the partially cured materials. Instead, the minimum in E' was used for the Mc calculations; this should result in Mc values that are more reflective of the as-cured material properties.

The Mc calculations assume a density of 1.0 g/cm^3 and should be viewed only as estimates, as the materials are continuing to cure in the rheometer. The E' data at 120°C provide a measure of the network properties after a defined amount of thermal exposure in the rheometer; for most of these samples, this additional exposure results in additional cure and/or loss of solvent, both of which will increase E'. Also calculated in *Table 1* is a cure ratio defined by E' at 120°C/minimum in E'. This ratio provides a relative measure of the amount of additional build in modulus (due to cure or solvent loss) that each sample experiences, with a larger ratio indicating that substantial property changes occurred in the rheometer.

The data in *Table 1* show that for the xylene-based formulations cured at ambient temperature and humidity, the T_g and minimum in E' increase with increasing cure time; this trend is expected as the degree of cure increases with increasing cure time. The decrease in the cure ratio with increasing cure time for the ambient-cured formulations provides additional evidence that the degree of cure increases with time. The similarity of the 6- and 21-day data, coupled with the fact that these data are lower than those observed for the heat-cured xylene-based sample, suggests there is a limit to the properties attainable at ambient temperature. The 50–55°C T_g for the 6- and 21-day ambient-cured samples suggests that these formulations are vitrified (or glassy) at ambient temperature, making it difficult to readily advance the degree of cure.

An overlay of the E' data as a function of temperature and cure time for the polyamide/epoxy samples (without xylene) cured at ambient, together with the data for the heat-cured sample, is shown in *Figure 4*. The midpoint T_g, minimum in E', Mc, E' at 120°C, and cure ratio data for these formulations are also summarized in *Table 1*. The trends observed for the xylene-based formulations are also seen for these 100% solids materials. Relative to *Figure 4,* the difference in data between the heat-cured and ambient-cured samples is considerably larger than the comparable difference for the xylene-based materials.

To more effectively compare the effect of solvent addition and cure time, an overlay of the E' data for all eight of the polyamide/epoxy samples is shown in *Figure 5*. In addition to the differences in midpoint T_g and the magnitudes of E' in the rubbery region, the solvent-based systems have broader E' vs temperature profiles compared to the corresponding 100% solids formulations. Other, more specific, observations from *Figure 5* suggest that:

- After two days of cure, the xylene-based formulation displays a 6°C lower midpoint T_g, higher Mc, and lower cure ratio compared to the 100% solids sample. The difference in midpoint T_g is relatively small compared to the ~15°C difference in onset T_g (as evidenced by the decrease in E' as the samples enter the T_g region). The presence of solvent appears to have depressed T_g, but afforded a higher degree of cure. At ~120°C the E' data for the two samples are comparable suggesting that they reach similar cure states.
- After six days of cure at ambient conditions, the xylene-based epoxy displays a 4°C higher midpoint T_g and higher crosslink

density (lower Mc) than the 100% solids sample. Similar to the trend observed after two days of cure, the onset T_g for the formulation with xylene is lower than the one without xylene, though the two six-day samples are more comparable in onset T_g than the two two-day samples. At ~120°C, the E' data for the two samples are comparable and higher than the E' data for the formulations cured for two days. The higher E' data at 120°C for the six-day samples compared to the two-day data could be the result of the additional cure afforded by the additional four days at ambient temperature resulting in more crosslinked (i.e., higher rubbery E') materials.

- After 21 days of cure, the xylene-modified and neat polyamide/epoxy formulations display midpoint T_gs that are nearly the same (52–53°C). These T_gs are relatively high compared to the cure temperature (ambient temperature) and result in systems that are vitrifying. Vitrification causes the reaction rates to decrease substantially so that long times are required to advance the degree of cure. The presence of xylene affords a higher crosslink density and lower onset T_g. The E' data at 120°C are comparable and higher than the corresponding data for the two- and six-day samples.
- The two 120°C heat-cured show a dramatic difference in midpoint T_g (~33°C), with the xylene-based formulation exhibiting the lower T_g (64°C). As was seen with the ambient-cured formulations prepared with xylene, the difference in the onset and midpoint T_gs for the heat-cured material made with xylene is greater than that observed for the neat material. Both heat-cured samples display cure ratios close to 1, suggesting that there is little additional cure occurring in the rheometer.

Thermal Data

The 1st and 2nd heating scan DSC data for the polyamide/epoxy formulation (prepared without xylene) immediately after mixing are shown in *Figures 6* and *7*, respectively. A summary of the key thermal data from the 1st and 2nd heating scans for this and the other 100% solids samples is provided in *Table 2*. As with the data in *Figure 6*, and the subsequent 1st scan DSC data, differences in how the baselines are drawn

FIGURE 6—1st heating scan DSC data for the polyamide/epoxy formulation (without xylene). The sample was analyzed immediately after mixing.

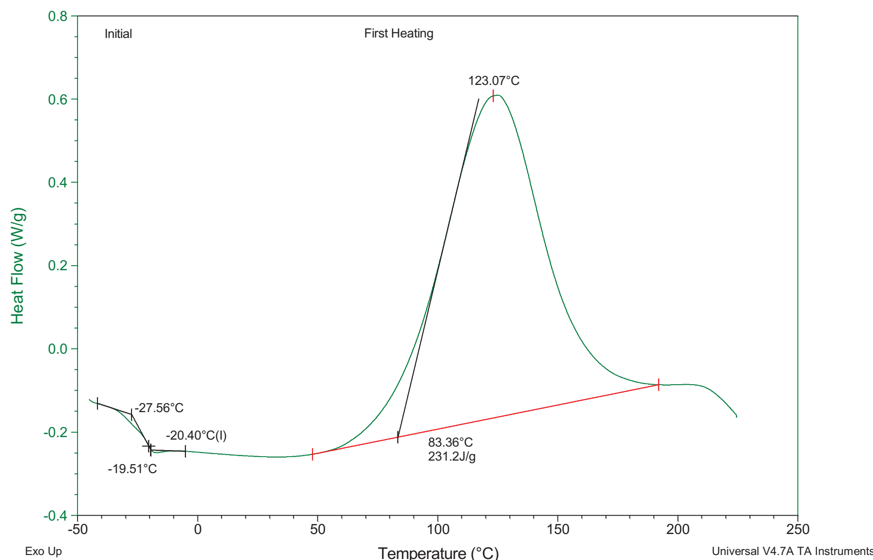


FIGURE 7—2nd heating scan DSC data for the polyamide/epoxy formulation (without xylene). The sample was analyzed immediately after mixing.

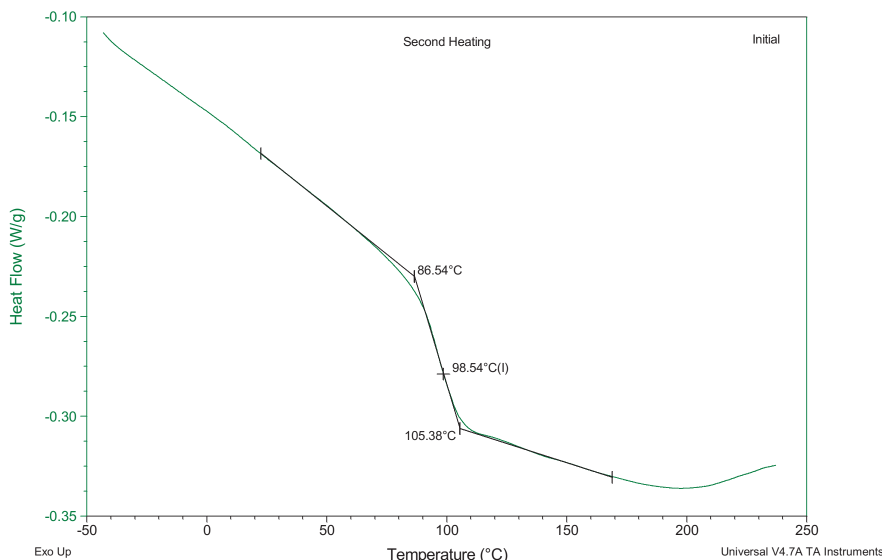


TABLE 2—Summary of the Key Thermal Data for the Polyamide/Epoxy Formulations Prepared without Xylene and the Heat-cured Polyamide/Epoxy/20% Xylene Formulation

SAMPLE	DSC HEATING SCAN	INFLECTION T_g [°C]	CURE EXOTHERM [J_g]	PEAK EXOTHERM TEMP. [°C]	EXTRAP. ONSET OF CURE [°C]
POLYAMIDE/EPOXY AFTER MIXING	1st	-20	231	123	83
	2nd	99	ND	ND	ND
POLYAMIDE/EPOXY AFTER 2 DAYS	1st	38	45	132	87
	2nd	99	ND	ND	ND
POLYAMIDE/EPOXY AFTER 6 DAYS	1st	49	44	132	85
	2nd	99	ND	ND	ND
POLYAMIDE/EPOXY AFTER 21 DAYS	1st	56	44	131	86
	2nd	96	ND	ND	ND
POLYAMIDE/EPOXY 120°C HEAT CURED	1st	48, 91	ND	ND	ND
	2nd	98	ND	ND	ND
POLYAMIDE/EPOXY/20% XYLENE 120°C HEAT CURED	1st	47, 65	ND	ND	ND
	2nd	67	ND	ND	ND

ND: None detected

impact the numerical values of the resulting tabulated data, especially for the cure exotherm. As a result, care must be taken not to over-interpret relatively small differences in thermal data.

The data in *Figure 6* show a T_g in the –20°C range (attributable to the two reactants) and an exotherm associated with cure over the 50 to 200°C range. Since the data were obtained immediately after mixing, the ~231 J/g exotherm reflects the total heat associated with cure. A single T_g of ~99°C and no residual cure exotherm are observed in *Figure 7*; since this is second scan data, this T_g is closer to the maximum T_g attainable for this system and is in good agreement with the T_g observed from the DMA experiments for the 100% solids heat-cured formulation.

The thermal data for the polyamide/epoxy sample cured two days at ambient temperature and humidity are shown in *Figures 8* and *9*. The 1st scan data indicate an inflection T_g of ~38°C and a residual cure exotherm of ~45 J/g. Based on the cure exotherm data in *Figures 6* and *8*, the degree of cure for this sample is ~81%. An apparent relaxation endotherm is also witnessed at the end of the glass transition region. Similar to the sample analyzed immediately after mixing (shown in *Figure 7*), the 2nd scan data in *Figure 9* indicate an inflection T_g of 99°C. The fact that the data in *Figures 7* and *9* are in agreement indicates that both materials result in comparable networks (at least with regard to T_g) and that the maximum attainable T_g does not appear to be dependent on the cure

FIGURE 8—1st heating scan DSC data for the polyamide/epoxy formulation (without xylene) after two days of cure at ambient temperature and humidity.

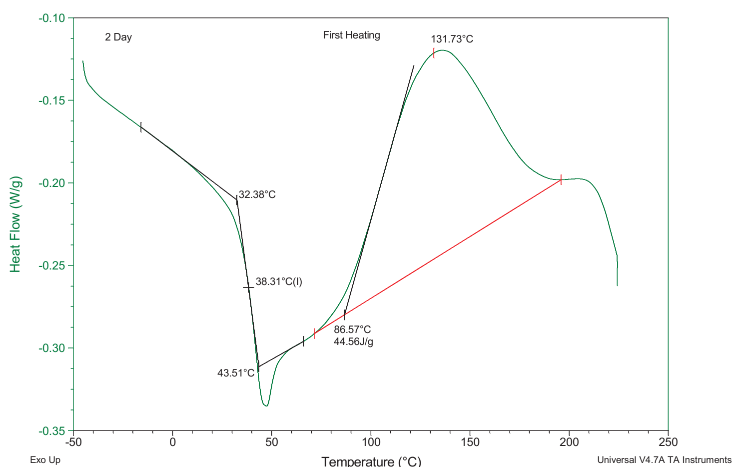


FIGURE 10—1st heating scan DSC data for the polyamide/epoxy formulation (without xylene) after six days of cure at ambient temperature and humidity.

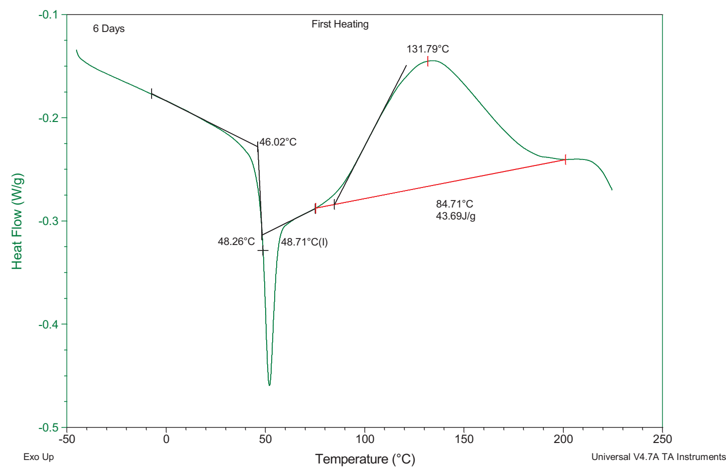


FIGURE 9—2nd heating scan DSC data for the polyamide/epoxy formulation (without xylene) after two days of cure at ambient temperature and humidity.

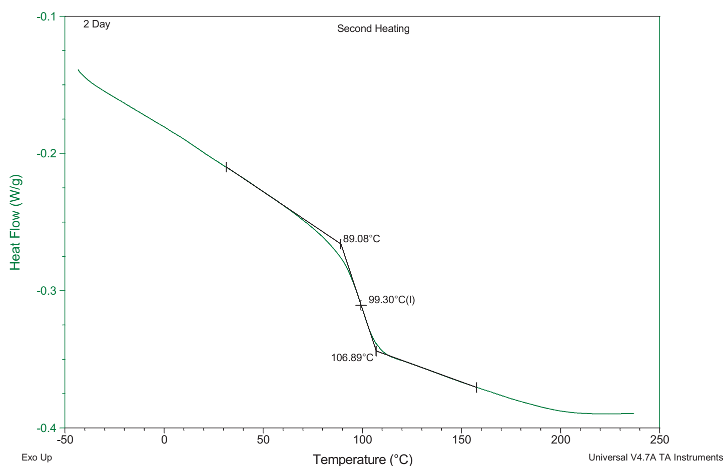
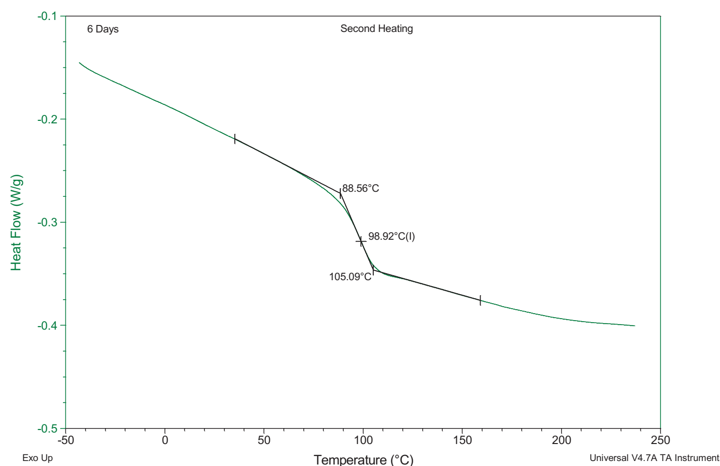


FIGURE 11—2nd heating scan DSC data for the polyamide/epoxy formulation (without xylene) after six days of cure at ambient temperature and humidity.



path, i.e., a ramp cure in the DSC vs two days at ambient temperature followed by a ramp cure in the DSC.

The DSC data after six days of cure at ambient temperature and humidity for the 100% solids sample are shown in *Figures 10* and *11*. Similar to the data in *Figure 8,* the 1st scan data exhibit a T_g, stress relaxation endotherm, and a residual cure exotherm. Relative to the two-day data, the T_g has increased, while the cure exotherm is comparable. The 2nd scan data indicate an inflection T_g of 99°C, the same as the data immediately after mixing and after two days of ambient cure.

The 1st and 2nd scan DSC data for the formulation cured 21 days at ambient temperature and humidity are shown in *Figures 12* and *13,* respectively. Relative to the data in *Figures 6, 8,* and *10,* the 1st scan T_g continues to increase, while the residual cure exotherm is about the same as two- and six-day data. The increases in the 1st scan T_g data with increasing cure time are in agreement with the DMA data in *Table 1*. The lack of change in the cure exotherm, coupled with the increase in the minimum E' (summarized in *Table 1*), suggests that DSC does not appear to be as sensitive to the latter stages of cure compared to DMA.

The DSC data for the 120°C heat-cured polyamide/epoxy formulation are shown in *Figures 14* and *15*. The 1st scan data indicate a small T_g around 48°C and a primary T_g of about 91°C. No residual cure exotherm is observed, which is consistent with the sample being fully cured prior to DSC analysis. The 2nd scan

FIGURE 12—1st heating scan DSC data for the polyamide/epoxy formulation (without xylene) after 21 days of cure at ambient temperature and humidity.

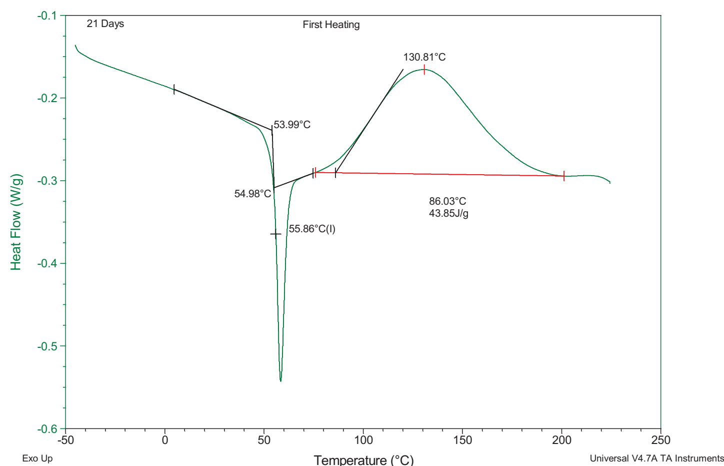


FIGURE 14—1st heating scan DSC data for the polyamide/epoxy formulation (without xylene) after heat curing at 150°C for three hours.

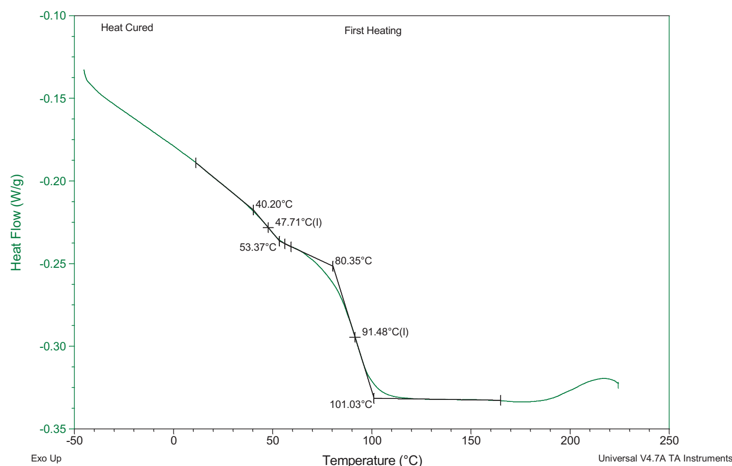


FIGURE 13—2nd heating scan DSC data for the polyamide/epoxy formulation (without xylene) after 21 days of cure at ambient temperature and humidity.

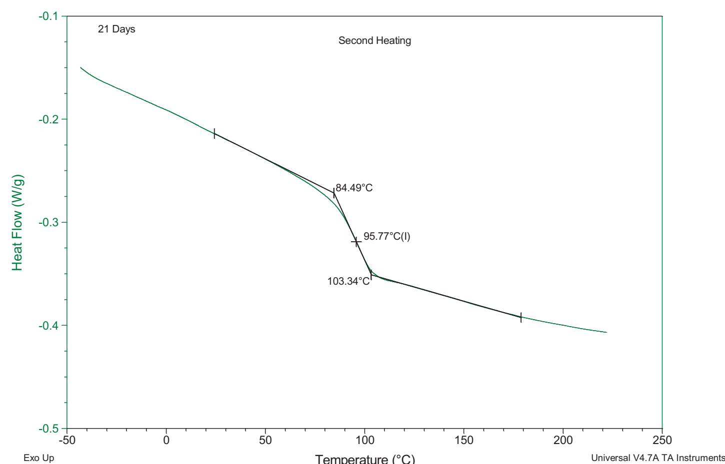


FIGURE 15—2nd heating scan DSC data for the polyamide/epoxy formulation (without xylene) after heat curing at 150°C for three hours.

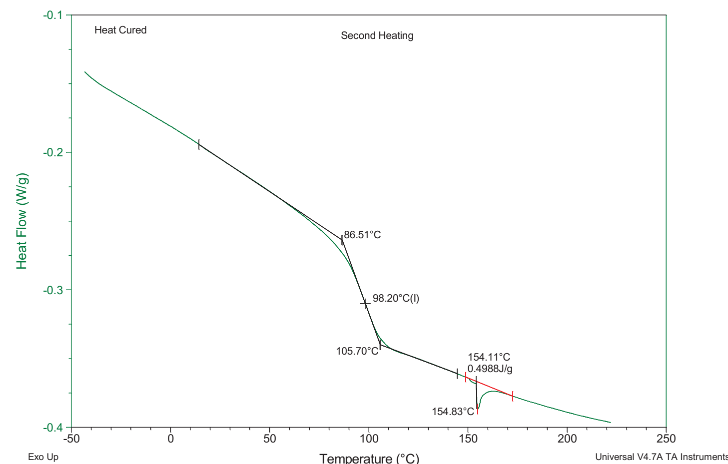


FIGURE 16—1st heating scan DSC data for the polyamide/epoxy/20% xylene formulation after heat curing at 150°C for three hours.

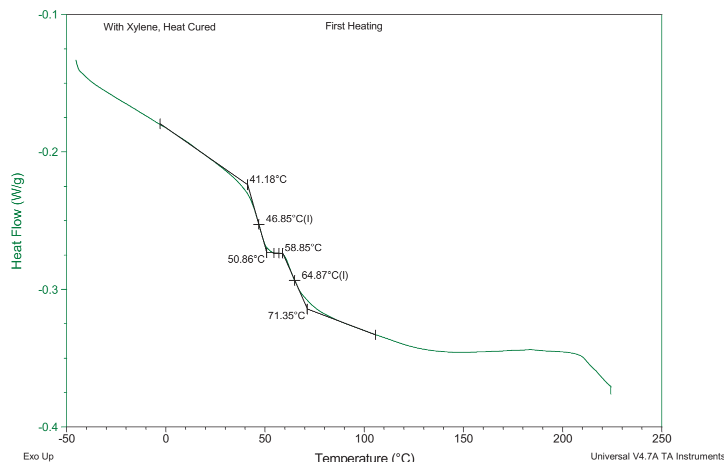
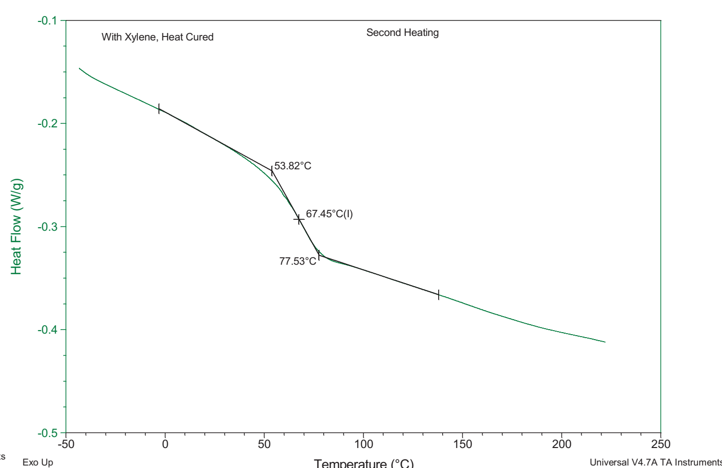


FIGURE 17—2nd heating scan DSC data for the polyamide/epoxy/20% xylene formulation after heat curing at 150°C for three hours.



T_g of 98°C is consistent with the prior 2nd scan DSC results. The endotherm at 155°C is likely an experimental artifact.

Inflection T_gs of 47 and 65°C are observed for the 120°C heat-cured polyamide/epoxy/20% xylene formulation; these data are shown in *Figure 16*. A residual cure exotherm is not evident. The impact of any residual xylene on the DSC data is not obvious. The 2nd scan DSC data for this material are shown in *Figure 17* and indicate an inflection T_g of 67°C.

The 2nd scan T_gs for the two heat cured samples (98°C for the 100% solids formulation, 67°C for the xylene-based formulation) are in very good agreement with the corresponding DMA data (97°C, 64°C). The relatively low ultimate T_g for the heat-cured sample prepared with xylene is either due to the plasticization of the crosslinked network by residual xylene or the presence of the xylene has somehow hindered or altered network formation.

Moisture-cured RTV Silicone Formulation

Figure 18 displays the tensile dynamic mechanical properties as a function of frequency for the moisture-cured RTV silicone after one hour of cure at ambient temperature and 30% RH. The rheological data are frequency-dependent, which is typical for a viscoelastic material. In particular, E' increases and tan(δ) decreases with increasing frequency. The decrease in tan(δ) indicates more solid-like (rather than liquid-like) behavior with increasing frequency. These rheological data are typical of those collected over the seven-day period.

Figure 19 displays the E' data as a function of frequency after 1 hr, 24 hr, and 7 days for both replicate specimens. The increase in E' with increasing cure time is indicative of additional cure. As might be expected, the largest increase in E' occurs early in the cure. In addition, the frequency dependence of E' decreases with increasing cure time indicating that a more elastic material is created with further cure. *Figure 20* presents the corresponding tan(δ) data over the seven-day cure period. The decrease in tan(δ) with increasing cure time corroborates the E' data shown in *Figure 20*.

These kinds of data provide an objective measure of the time required to achieve different degrees of cure, as well as insight into how the material properties change with time. Similar studies could be conducted at other environmental conditions where it would be expected that experiments conducted at higher RHs would result in a faster cure of the moisture-cured RTV material.

Polyetheramine/Epoxy Blends

Figure 21 is an overlay of the E' and tan(δ) data for the three cured PEA Low/PEA High/epoxy formulations. The increase in T_g and crosslink density (as evidenced by the E' data in the rubbery region) with increasing PEA Low level is evident. This is not surprising considering that PEA Low has a smaller molecular weight (and lower equivalent weight) and yields a tighter network compared to PEA High-based formulations.

The E' data for the 60%/40%, 70%/30%, and 80%/20% PEA Low/PEA High blends cured with epoxy resin as a function of immersion time are shown in *Figure 22*. The magnitude of E' prior to the introduction of the water follows the expected trend, with the 80%/20% blend exhibiting the highest modulus at ambient temperature. The immersion data indicate a decrease in E' with increasing immersion time that is due to the uptake of water into the crosslinked networks. This decrease in E' is more pronounced as the level of PEA High in the formulation increases. One explanation for this is that by increasing the average molecular weight between crosslinks of the network, it is easier for water to diffuse into the polymer network, causing the modulus to decrease with increasing immersion time because of plasticization.

While these experiments were performed with water at ambient temperature, organic solvents, as well as temperatures other than ambient could be used to understand the solvent resistance of coatings. Immersion experiments performed at a higher temperature or with thinner films would likely yield comparable results on a shorter time scale. These immersion experiments are particularly useful as they collect

FIGURE 18—Tensile dynamical properties as a function of frequency for the moisture-cured RTV silicone after one hour of cure at ambient temperature and 30% RH.

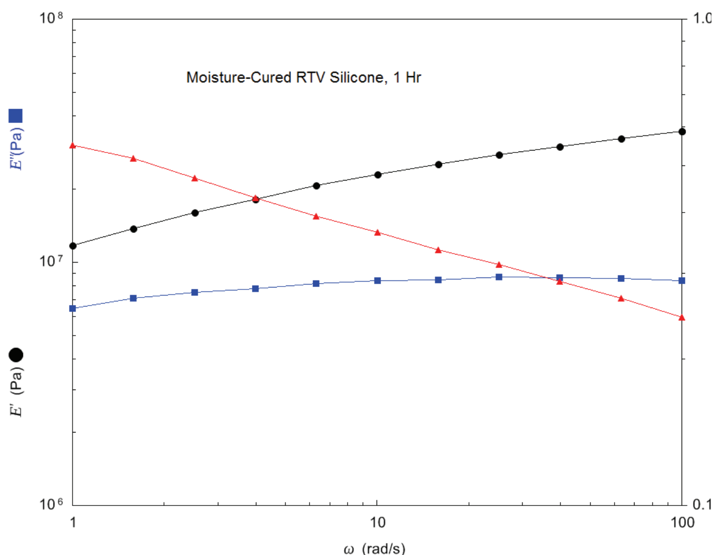


FIGURE 20—Overlay of the tan(δ) data for all of the moisture-cured RTV silicone specimens as a function of frequency at ambient temperature and 30% RH.

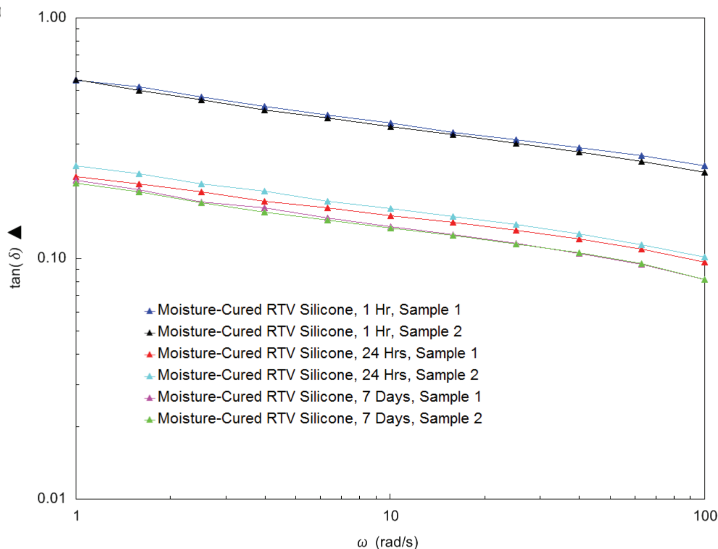


FIGURE 19—Overlay of the tensile storage modulus (E′) data for all of the moisture-cured RTV silicone specimens as a function of frequency at ambient temperature and 30% RH.

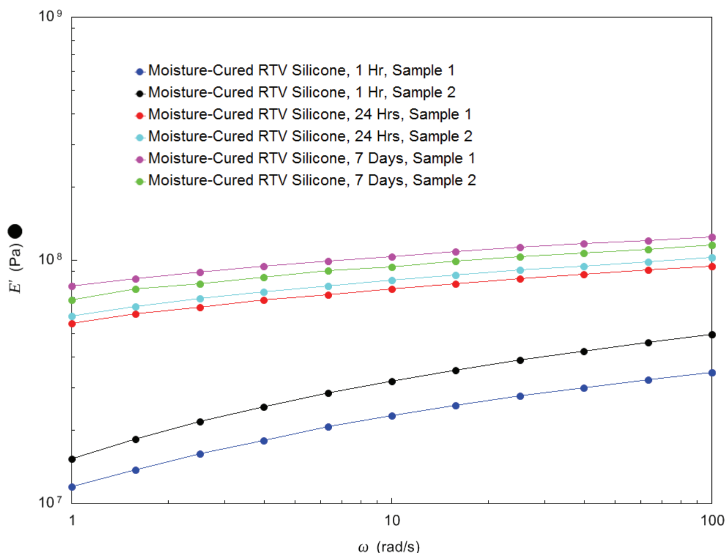
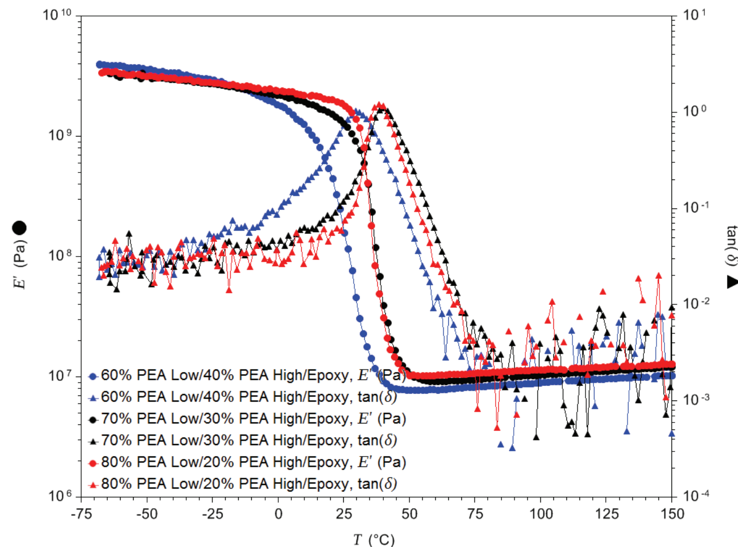
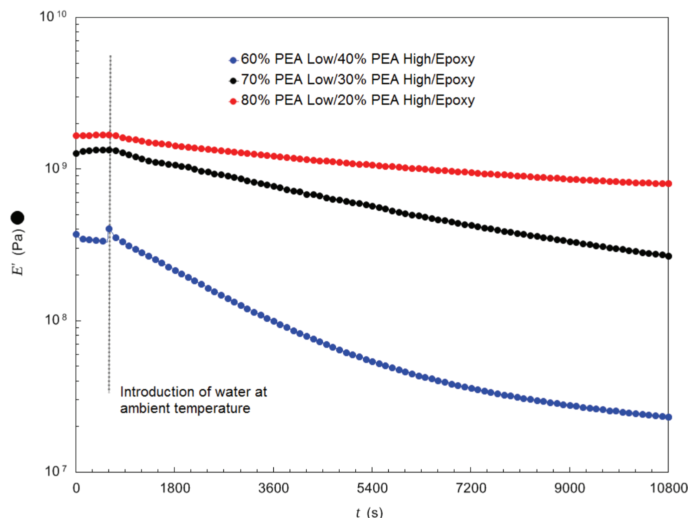


FIGURE 21—Overlay of the tensile storage modulus (E′) and tan(δ) data for the three polyetheramine/epoxy formulations. The formulations were heat cured at 150°C prior to analysis.



data in real time and provide kinetic-type information and alleviate the issues associated with traditional solvent resistance experiments, namely the need to remove and handle materials from the immersion medium and load them into a rheometer without excessive deformation. Of course, if the time required for a coating to experience the impact of a solvent is particularly long or requires exposure conditions that cannot be accommodated by the immersion fixture and rheometer, the more traditional approach of immersing and removing specimens for testing needs to be employed.

FIGURE 22—Tensile storage modulus (E′) data as a function of immersion time in water at ambient temperature for the three polyetheramine/epoxy formulations. The formulations were heat cured at 150°C prior to analysis. Each tick on the x-axis is equal to five minutes.



SUMMARY

The rheological and thermal properties of a polyamide-cured epoxy coating (prepared with and without xylene)

and a moisture-cured RTV silicone coating were characterized during cure using DMA and DSC. For both coatings, substrates that enabled the analysis of free films were used. DSC measurements were limited to materials that had relatively little solvent, as the endotherm associated with the evolution of relatively large amounts of solvent dominated the thermal curves, making it impossible to determine T_gs and residual cure exotherms.

Both the polyamide/epoxy (100% solids) and polyamide/epoxy/20% xylene formulations exhibit increases in T_g with increasing cure time. For comparable cure times at ambient temperature and humidity, the presence of solvent results in lower onset T_gs and lower Mcs. Dynamic mechanical and DSC data on 120°C heat-cured samples of the xylene-modified and 100% solids formulations indicate that the presence of xylene results in a significantly lower T_g data (~97 vs 64°C); part of this may be due to the difficulty of xylene to diffuse out of the relatively thick coating that was used.

For the silicone-based coating formulation, the DMA data show a steady increase in E' over the course of a seven-day cure at ambient temperature and 30% RH, coupled with an increase in the elastic character of the material with increasing cure time.

Two polyetheramine curatives, one with a relatively low molecular weight (PEA Low) and one with a relatively high molecular weight (PEA High), were used to prepare three epoxy-based coatings of varying crosslink density. For each formulation, decreases in E' as a result of immersion in water were measured in situ as a function of time using an immersion fixture. Of the three networks, the one with the largest Mc (60% PEA Low/40% PEA High/Epoxy) exhibits the largest decrease in E'; this is likely due to the relative ease with which water can penetrate and plasticize the matrix. This approach to evaluating the solvent resistance of coatings avoids the handling issues associated with traditional immersion studies that rely on periodically removing and testing a sample that has been immersed.

By measuring rheological and thermal properties as a function of cure time, it is possible to understand the rate with which properties develop and the transformation from the liquid to the solid state. It is particularly useful when these types of studies can be compared against the performance of a control formulation. The analytical approaches shown here can be extended to other coatings systems and can be complemented by techniques that suit the specific needs of the coatings technologist. ❊

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