

Better Thermal, Mechanical and Dielectric Properties of Cured Polyimides Using Low Pressure Vacuum Cure Processing

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Abstract— In this paper, to meet the demand placed on Polyimide materials in Fan Out Wafer and Panel Level Processing applicable to Heterogeneous Integration, thermal, mechanical, and dielectric properties were studied for different types of Polyimide and Poly-Benz-Oxazole (PBO) materials, such as HD-4100, HD-8820 and HD7110, as a function of different process parameters, under atmospheric and vacuum process conditions. Vacuum cure results in higher thermal stability with lower outgassing in HD-4100 and HD-8820 films. Vacuum cure of HD-4100 and HD-7110 appears to increase the dielectric strength, but no similar trend is seen for HD-8820. These results are consistent with the assumption that cure under vacuum reduces the amount of volatile and volatilizable material remaining in the film after the cure process.

Keywords—*Heterogeneous Integration (HI), FOWLP, FOPLP, Polyimide, Vacuum Cure.*

I. INTRODUCTION

In the past few years, tremendous effort has been devoted to enhancing the capabilities of high-density backend processing by increasing the number of redistribution layers (RDLs), shrinking the dimensions of the metal lines' width and spacing (L/S), and reducing the pad size and pitch. While this effort is on-going either for high performance or lower cost in backend processing, different focus is given simultaneously on 5G high frequency connectivity, big data analysis, artificial intelligence, augmented and virtual reality, and autonomous driving/vehicles. Consequently, during the next few years, we also expect to see an increased level of Heterogeneous Integration (HI). Heterogeneous Integration uses packaging technologies to integrate dissimilar chips with different functions from a wide variety of fabless houses, foundries, wafer sizes, and feature sizes into a system and sub-system. With the advancement of Heterogeneous Integration, multi-layer RDLs are used to

connect these dissimilar chips on organic, glass, silicon or fan-out substrates [1]. Moreover, the need for faster development cycle times with higher reliability and lower cost adds further challenges for each individual process. Given this added complexity, dissimilar chips, and different substrate size and materials, the importance of polymer, epoxy, underfill materials, or Photo Imageable Dielectric (PID) curing is significant in yielding not only lower cure temperature and shorter cure time resulting in lower thermal budget, but also resulting in better film properties. While there are a number of different polymer cure processes, selection of the specific process can have a significant effect on the quality and performance of cured polymers, applicable to the Fan Out Wafer Level Packaging (FOWLP) or Fan Out Panel Level Packaging (FOPLP) Multi-level Metallization Process.

In this paper, mechanical, thermal, physical and dielectric properties were studied for different types of Polyimide and PBO materials as a function of different process parameters of time and temperature under sub-atmospheric process conditions using the YES VertaCure system.

II. EXPERIMENTAL

A. Trend towards Low Temperature Polyimides and Related Cure Processes

Fig. 1 shows the trend of lowering cure temperature required for different substrates as well as different applications. In addition to temperature, dwell time and atmosphere can impact how a material cures. At reduced pressure, water and solvent are drawn out of the bulk polymer at much lower temperatures than an atmospheric pressure cure. Thus cure at reduced pressure will change the film composition during cure relative to cure at atmospheric pressure. In addition to the effect of pressure, partial pressures of specific gases can impact the cured film properties. At atmospheric pressure, oxygen content above 100 ppm can cause oxidative side-reactions that embrittle the

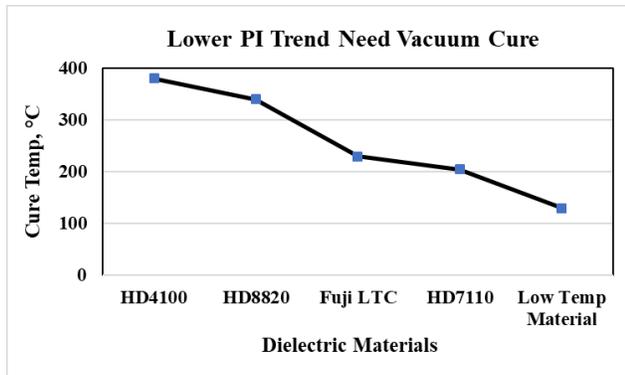


Fig. 1. Trend of Cure Temperatures of Polyimide Dielectrics

cured films. High relative humidity during the initial thermal ramp can cause some hydrolysis of the backbone amide groups in the Polyimide or PBO precursor polymers. This hydrolysis will result in a reduction of molecular weight and lower tensile strength. At the beginning of the cure cycle, Polyimide films will typically contain 15 - 20 wt. % solvent. The rate at which the solvent is removed can impact film quality and properties. Overly rapid removal of solvent from the surface of the film can inhibit evaporation of solvent and water vapor from the bulk of the film. This skin effect will cause wrinkles, cracks, discoloration and outgassing on subsequent vacuum steps such as metallization. At higher temperatures, efficient removal of solvent and other volatiles is critical to incorporating better molecular packing to help increase dielectric strength.

B. Selection of Polyimides and Related Mechanisms

Photodefinable Polyimide formulations (PSPI) were developed in the 1980's which formed Polyimide films when cured above 300°C [2]. Typically these formulations consisted of a solution of polyamic acid modified with unsaturated (hence cross-linkable) functionality either as covalently bound ester or as ionic salt, along with photoinitiator, additional crosslinker and adhesion promoter. After coating a substrate and baking to remove much of the solvent, the coated films were exposed to ultraviolet (UV) light through a pattern mask. Light exposure initiated chain polymerization of the unsaturated moieties. These cross-linked regions of the film were much less soluble in solvent developer than the unexposed regions, so that a negative-tone image was formed after development.

During the cure process, several types of volatile species evolve from these negative tone PSPIs. Residual solvent retained in the film after soft bake will evaporate at a rate determined by the cure temperature, the boiling point of the solvent, and the amount of hydrogen bonding between the solvent and the Polyimide. Ring closure to form Polyimide will generate water vapor or break the ester linkage between the Polyimide and the crosslinked network. At 300°C and above, thermal decomposition of the crosslinked network will form a variety of lower molecular weight species which may volatilize out of the film.

In the last few years, negative-tone PSPI were introduced which can be cured well below 300°C [3, 4]. In these systems, the Polyimide and the cross linker chemistries are chosen to enable efficient cyclization at low temperature and to obtain desired properties without thermal decomposition of the crosslinker. Compared to standard PSPIs, these low cure-temperature systems evolve significantly fewer volatiles during cure. The main volatile components from these systems are residual solvent, water of imidization and photoinitiator decomposition products.

Photodefinable polybenzoxazoles (PBO) are prepared from solutions containing polyhydroxyamides, adhesion promoter and photoacid generator [2]. PBOs are positive-tone: UV exposure generates acid which increases the solubility of the film to aqueous base relative to unexposed areas. Cure of the PBO results in solvent loss, ring-closure with evolution of water and thermal decomposition of the photopackage with accompanying loss of volatiles.

Thickness loss during cure parallels the amount of volatiles that come out of the films during cure. Standard cure PSPI have the highest cure shrinkage followed by PBOs; low cure temperature PSPI have the least shrinkage of these systems.

C. Experimental Process

HD-4100, HD-8820 and HD-7110 formulated resins were provided by HD MicroSystems. Formulations were coated onto 6" semi-grade silicon wafers using automated track systems for coating, soft baking and development. In those cases where the film needed to be released from the wafer after cure, silicon wafers with a coating of cured PI-2611 were used as the substrate. Coat, bake, exposure and development conditions for the three formulations are listed in Table I.

TABLE I COAT, BAKE AND DEVELOPMENT CONDITIONS

Formulation	HD-4100	HD-8820	HD-7110
Spin speed (rpm)	1520	1250	2280
Spin time	45s	30s	30s
Bake 1	90°C, 120s	120°C, 180s	105°C, 120s
Bake 2	110°C, 120s		115°C, 120s
Exposure	500 mJ/cm ² i-line	700 mJ/cm ²	500 mJ/cm ² i-line
Developer	Cyclopentanone	TMAH, 2.38% in H ₂ O	Cyclopentanone
Development Process	Spray 30s	Puddle 2 x 33s	Puddle 3 x 5s
Recommended Cure Temperature	375°C	320°C	205°C

The mechanical, thermal, physical and dielectric properties were studied as a function of different process parameters of time and temperature under sub-atmospheric process conditions using the YES VertaCure system. The YES VertaCure vacuum cure system is capable of processing 50 wafers per batch per process module. YES VertaCure system provides 5-zone temp control with <1% temp uniformity. An automatic pressure control valve (APC) was used to maintain the process pressure during the ramp and dwell segments of the runs. The control samples from HD MicroSystems were cured at 760Torr using an atmospheric cure oven. Other samples were cured with a

YES VertaCure system at 400Torr, 200Torr, 100Torr or 50 Torr to determine the impact of pressure. In addition, some of the samples were cured for shorter times at the base pressure of 200Torr to study the impact of cure time.

10 mm wide strips for tensile testing were photo-exposed on an Ultratech AP200 stepper. The other coatings made from HD-4100 or HD-7110 were "blanket" exposed with an OAI mask aligner. Both patterned and un-patterned films were processed through the development step.

Tensile testing was carried out using an MTS Model 1122 frame equipped with rubberized grips, a 50 lb load cell and TestWorks software. Initial grip spacing (gauge length) was 20 mm and crosshead speed was 5 mm/min. Ten specimens were tested from each cured film; data from the five specimens with the highest elongation to break were averaged to obtain modulus, strength and elongation values.

Glass transition temperature (T_g) and coefficient of thermal expansion (CTE) were measured with a SII Exstar 6000 TMA. Three millimeter wide test specimens were held at 40 mN tensile force as the temperature was ramped at 10°C/min. Specimens were 1) heated to either 180°C (HD-7110) or 250°C (HD-8820 and HD-4100), 2) cooled to room temperature and 3) heated to 400°C. Data were analyzed from the second heating ramp.

Residual film stress was determined using a Frontier Semiconductor FSM 500TC operating at room temperature. The wafers used for film stress measurement were first measured for wafer bow in the uncoated state. After coating and curing the films, the bow was measured a second time. The change in wafer bow along with knowledge of the wafer thickness and modulus as well as the film thickness were used to calculate residual stress in the films.

Thermal decomposition measurements on free-standing films were made with a TA Instruments Q500 TGA. ~10 mg specimens were heated at 20°C/min from room temperature to 540°C. 1% and 5% weight loss values were determined using the sample weight at 135°C (after water vapor is desorbed) as the 0% weight loss value.

For dielectric testing, 64 mm diameter coupons were cut from free-standing films. To measure dielectric constant (D_k) and dissipation factor (D_f), the coupons were placed into a copper 10GHz cavity resonator at ambient temperature and humidity. Data were collected with a Network Analyzer and analyzed using Matlab to calculate D_f and D_k .

Breakdown voltage was determined by placing the test coupons between brass electrodes connected to a HYPOT Dielectric Withstand tester. Voltage was increased at 1.67V/s to a maximum voltage of 5kV and breakdown was taken as the voltage at which the current was 20mA.

III. RESULTS AND DISCUSSIONS

Tensile, thermomechanical, thermal stability, outgassing, imidization, and dielectric properties were extensively studied with respect to cure process parameters.

A. Tensile Properties

The modulus and strength of a film are important indicators of the ability of the film to absorb and withstand the stresses that

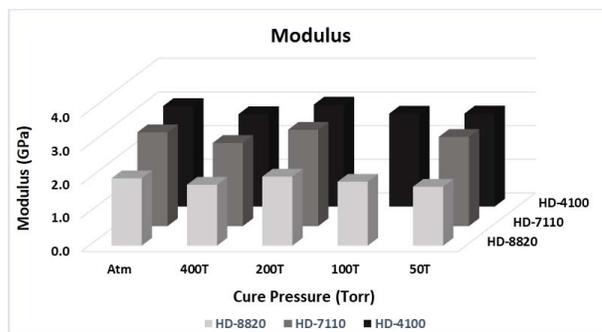


Fig. 2(a). Tensile moduli as a function of cure pressure for HD4100, HD8820 and HD7110

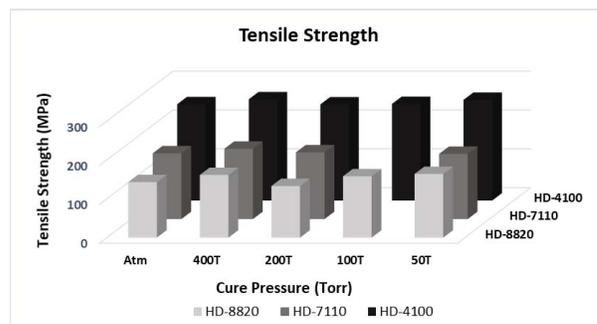


Fig. 2(b). Tensile strength as a function of cure pressure for HD4100, HD8820 and HD7110

occur at the interface between the film and metallic conductors or inorganic dielectrics. As shown in Fig. 2(a), the Polyimide films (from HD-4100 and HD-7110) exhibited tensile moduli around 3 GPa, while the PBO films (from HD-8820) had moduli around 2 GPa. Films from HD-4100 had tensile strength of ~250 MPa. Films from HD-8820 had tensile strength of ~150 MPa, slightly lower in tensile strength than films from HD-7110, as shown in Fig. 2(b). The data shown are averages of five or ten tensile specimens. Over the cure pressure range from ~760 Torr to 50 Torr, we do not find a significant difference in either modulus or tensile strength for any of the three materials that were studied.

B. Thermomechanical Properties

During production and assembly of the chip, as well as during use, the polymer films are subject to numerous thermal excursions. If the film is heated above its glass transition temperature (T_g), the polymer will change from a glassy state to a rubbery state. This transition is accompanied by a large increase in specific volume and a decrease in the modulus. Below the T_g , an unstressed film will expand as it is heated and contract as it is cooled. We measured the thermal expansion coefficient (CTE) and T_g of the films; the results are shown in Fig. 3(a) and Fig. 3(b) respectively. The CTE of films made from HD-8820 and HD-4100 were ~50 ppm/°C while the films made from HD-7110 had somewhat higher CTE of ~65 ppm/°C. The data do not show a dependence of CTE (ppm/°C) on process pressure during cure. Films made from HD-4100

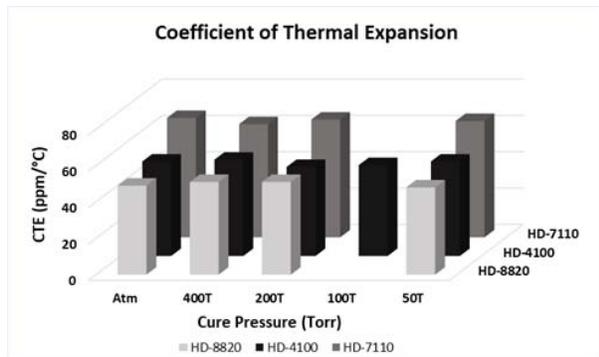


Fig. 3(a). CTE as a function of cure pressures for HD-4100, HD-8820 and HD-7110

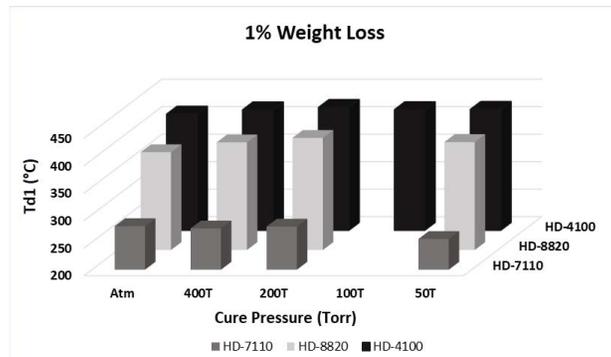


Fig. 4(a). 1% Weight Loss as a function of cure pressures for HD-4100, HD-8820 and HD-7110

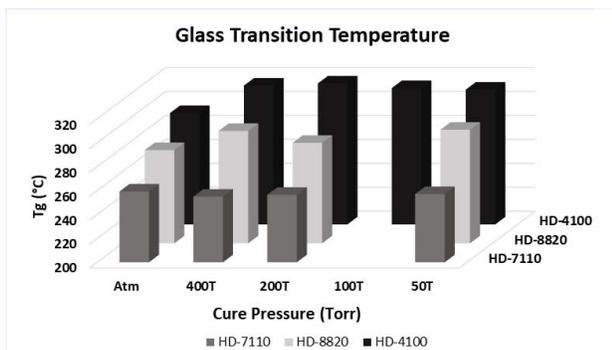


Fig. 3(b). Tg as a function of cure pressures for HD-4100, HD-8820 and HD-7110

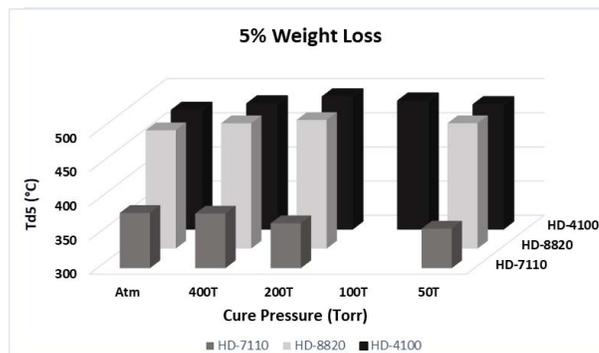


Fig. 4(b). 5% Weight Loss as a function of cure pressures for HD-4100, HD-8820 and HD-7110

and HD-8820 which were cured under vacuum have 15-20°C higher Tg than the films cured at atmospheric pressure; there is no obvious effect of lowering cure pressure from 400 to 50 Torr. HD-7110 films do not show any dependence of Tg on pressure during cure.

Residual Film Stress is a measure of the interfacial stress between a film and the substrate after cure. Highly stressed films cause the substrate to bow and warp. Excess stress can cause film delamination and excessive bowing can cause problems with wafer handling during processing as well as die bonding. Residual Film Stress values are within a narrow range (39 - 43 MPa) for all three materials at all tested process conditions.

C. Thermal Stability Studies

Thermogravimetric Analysis (TGA) measures weight changes at elevated temperature. The changes in weight are due to loss of material in the film which is volatile at high temperature. Several types of volatile species contribute to weight loss during heating:

- Absorbed water vapor as well as any absorbed atmospheric gases will volatilize below 150°C
- Solvent should be removed during the cure process, but some solvent can remain in the film due to hydrogen

bonding and will evolve from the film when heated above the cure temperature

- If the Polyimide or PBO precursors are not completely cyclized during cure then some additional cyclization can occur with release of water vapor.
- During the cure cycle, photoinitiators and crosslinkers can thermally decompose. Decomposition products which are volatile at cure temperature will be removed during the cure. When the sample is heated in the TGA above the cure temperature, additional volatile species will come out of the film.
- When the films are heated above the cure temperature, some of the components will undergo thermal decomposition and volatilize from the film.

In Fig. 4(a) and 4(b), we show the temperatures at which 1% (Td1) and 5% (Td5) of the film weight are lost. Td1 and Td5 are higher for HD-4100 and HD-8820 films cured under vacuum. HD-7110 films do not show higher thermal stability when cured under vacuum; in fact lower cure pressure seems to result in a reduction in Td1 and Td5 for this low cure-temperature material.

D. Outgassing under Different Conditions

Gas chromatography-mass spectrometry (GC-MS) was used to identify the volatiles from different samples after the same samples were cured at atmospheric pressure and 200Torr

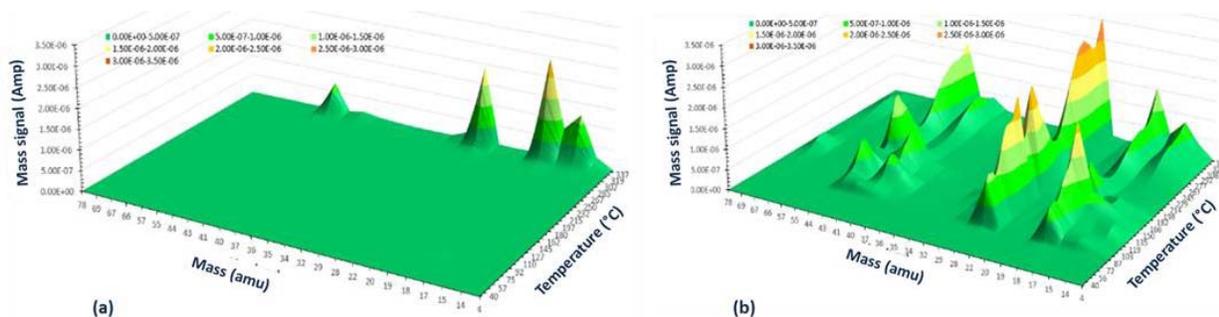


Fig. 5: Outgassing of (a) YES vacuum cured and (b) atmospheric cured HD-4100 film. No outgassing was observed until 300°C anneal for 5(a).

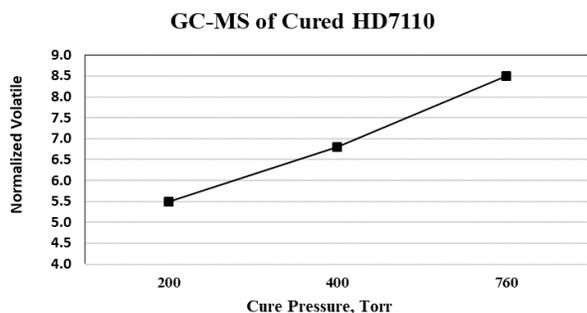


Fig. 6. Volatile outgassing from films cured at 200Torr, 400Torr and 760Torr pressure.

pressure. Outgassed species were collected for GC-MS analysis. The outgassing of NMP volatiles were much higher for atmospheric cured film in case of HD-4100 as shown in Fig. 5(a) and 5(b).

Similar studies were carried out for HD-7110 cured at 205°C at atmospheric and 200Torr process pressure. GC-MS analysis showed that film volatiles of NMP, the major solvent in HD-7110, are much lower in vacuum cured films compared to atmospheric pressure cured film, as shown in Fig 6.

E. Extent of Imidization Using FTIR

The FTIR spectra of cured Polyimides of HD-4100, HD-7110 and HD-8820 under vacuum or atmospheric conditions were analyzed to compare the extent of imidization. For HD-4100, the characteristic absorption peaks of the imide carbonyl group (C=O) near 1777 and 1714 cm^{-1} were observed, indicating the same degree of imidization using vacuum or atmospheric curing. FTIR analysis of vacuum cured Polyimides and atmospheric cured Polyimide exhibit identical profiles, confirming the similar compound structure after curing.

For HD-7110, the characteristic absorption peaks of the imide carbonyl group near 1778 and 1716 cm^{-1} were also observed, indicating the same degree of imidization whether using vacuum or atmospheric curing. It is noted that the peak intensity near 3660 – 3670 cm^{-1} related to O-H (or moisture) is

higher for the atmospheric cure condition, which is consistent with the volatile amount trends shown in Fig. 6.

For HD-8820, the absence of characteristic absorption peaks of amide C=O near 1650 cm^{-1} and amide N-H peak near 1537 cm^{-1} in the polymer backbone indicated again the same degree of imidization in vacuum or atmospheric curing conditions. Identical profiles were observed at pressures of 400 torr, 200 torr and 50 torr.

F. Dielectric Properties Analysis

The dielectric constant (Dk) and dissipation factor (Df) of the dielectric film affect signal propagation in the conductive traces surrounded by the dielectric. Lower Dk supports higher transmission speed while lower Df improves signal integrity.

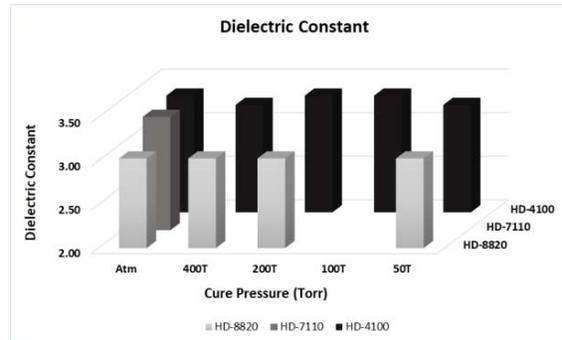


Fig. 7 (a). Dielectric Constant (Dk) of HD-4100, HD-8820 and HD-7110 films cured at different pressures.

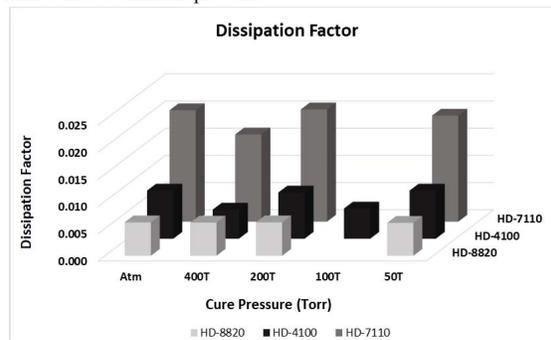


Fig. 7 (b). Dissipation Factor (Df) of HD-4100, HD-8820 and HD-7110 films cured at different pressures.

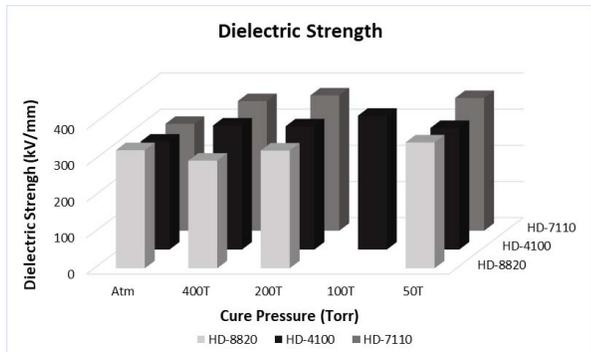


Fig. 7(c). Dielectric Strength of HD-4100, HD-8820 and HD-7110 films cured at different pressures.

Measured values for Dk for HD-4100 and HD-8820 films appear in Fig. 7(a). The data showed no effect on Dk of atmospheric pressure during cure; Dk for HD-4100 was ~3.3 and Dk for HD-8820 was ~3.0. The Dk results for HD-7110 films are not shown because the values obtained were inconsistent; a Dk of 3.3 has been reported [3]. Df values for the three materials, shown in Fig. 7(b) were not affected by vacuum cure. Df values ranged from 0.006 for HD-8820 and 0.009 for HD-4100 to 0.021 for HD-7110. Fig. 7(c) shows that dielectric strength values for HD-4100 and HD-7110 films cured under vacuum were approximately 10% higher than films cured at atmospheric pressure. No such effect of cure conditions was seen for HD-8820.

IV. SUMMARY

As noted above, vacuum cure results in higher Tg, Td1 and Td5 with lower outgassing in HD-8820 and HD-4100 films. These results are consistent with the assumption that cure under vacuum reduces the amount of volatile and volatilizable material remaining in the film after the cure process. These volatile species will act as plasticizers which reduce Tg and the loss of these volatiles during TGA analysis will lower Td1 and Td5. Vacuum cure of HD-4100 and HD-7110 appears to increase the

dielectric strength, but no similar trend is seen for HD-8820. HD-7110 cured films do not show an increase in Tg or reduction in Td under vacuum cure. It is expected that vacuum cure reduces the solvent content versus atmospheric cure in HD-7110, so one might expect some change in Td as a function of vacuum. However, unlike HD-4100, cure of HD-7110 at 205°C is not expected to cause significant thermal decomposition of the film components. These components do begin to undergo thermal decomposition at ~260°C, which results in the lower Td1 and Td5 for HD-7110. These decomposition products are the main factor in determining Td.

Of the three materials in this study, HD-4100 film properties appear to benefit most from vacuum cure: Tg, Td and dielectric strength are increased and outgassing decreased while the values of other properties are unchanged from the atmospheric cure process. HD-8820 films exhibit some increase in Tg and Td with vacuum cure and otherwise stable performance vs. atmospheric cure. HD-7110 films, with their low volatile output during cure, are least affected by vacuum cure.

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