

Examination of a Standardized Test for Evaluating the Degree of Cure of EVA Encapsulation (#1066/0731)

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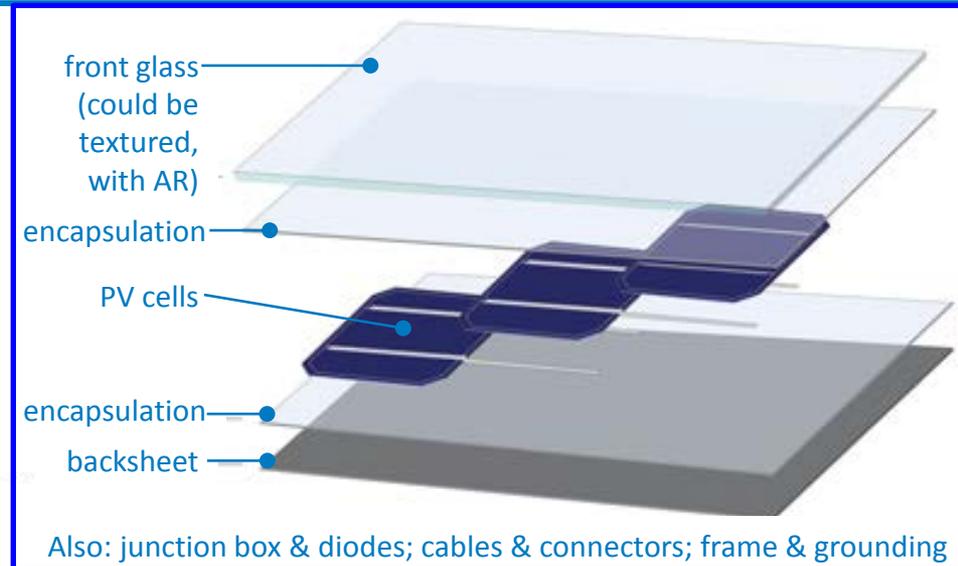


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This presentation contains no proprietary information
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Background: PV Modules, EVA, and Lamination

- PV modules are increasingly complex multi-component products, assembled using vacuum lamination.
- Ethylene-co-vinyl acetate (EVA) encapsulation attaches components (glass, cell, backsheet) together, when it is cross-linked.
- The lamination temperature activates peroxide-initiated thermosetting (“curing”).
- Curing then activates primer additive(s), facilitating adhesion.
- Module manufacturers seek a minimum degree of cure to ensure mechanical integrity.
- The cost of manufacturing (lamination) motivates using the minimal time and temperature.



“Exploded” view of components used in the historically most-common PV module configuration: glass/backsheet.

http://www.viridiansolar.co.uk/Assets/Images/Technical/laminate_small.jpg

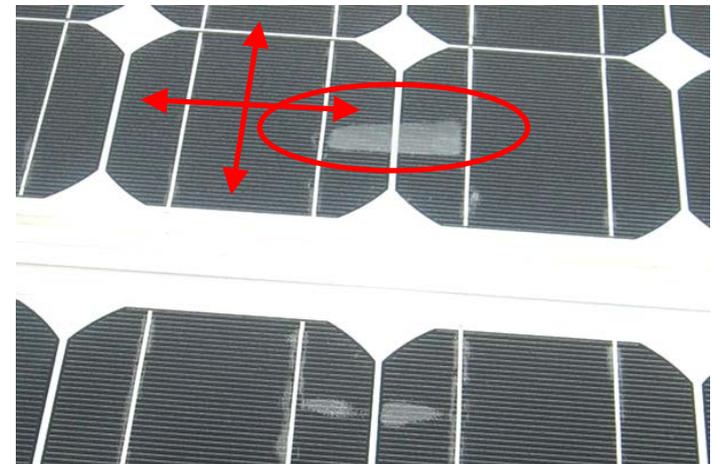


Photo of undercured module, fielded for ~1 year. Problems can include *displaced components* and *delamination*.

Motivation for a Degree of Cure Test Standard (IEC 62755, from NWIP #655)

A test standard helps material or module manufacturers to:

- Verify the cross-linking additive is **present** and has **not expired**.
- Facilitate **quality and process control** of lamination.
- **Assess uniformity** of the EVA formulation within a roll.
- **Compare variation** of the EVA formulation from roll to roll.

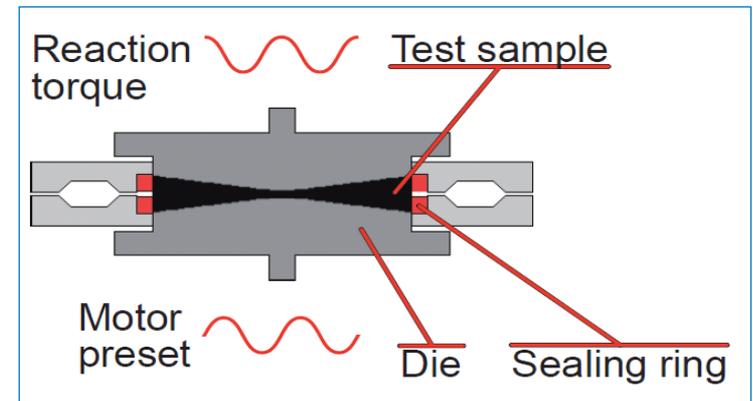
No specified pass/fail criteria. Pass/fail may be set by the user.

The standard may be applied to:

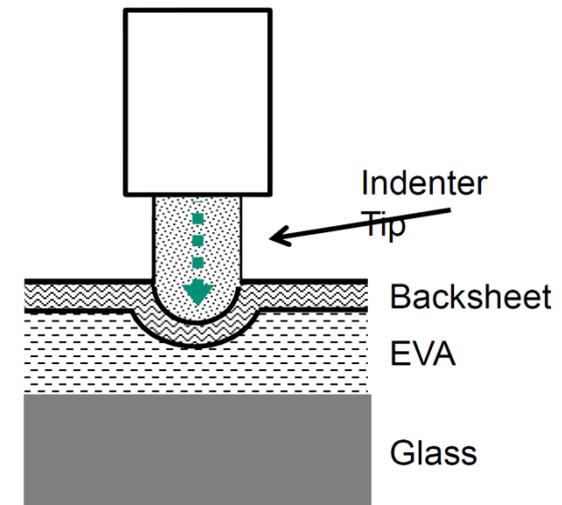
- Uncured or recently cured **EVA sheet**.
- Uncured or recently cured **EVA from PV modules**.
- **Other thermosets**. Details in the standard are tailored to EVA.

Possible Methods to Assess Degree of Cure, G

- Rheometry, *e.g.*, DMA
- Rheometric cure metering
 - ISO 6502, ASTM D5289.
 - *Direct assessment of the key mechanical characteristics.*
- **Gel content**
 - ISO 10147, ASTM D2765
- Swell ratio
 - ASTM D2765
- **DSC**
 - Residual enthalpy method, *e.g.*, ASTM E2160
 - Melt/freeze method
- **Indentation**
 - *Performed on backsheet side, nondestructive.*
 - *Presently being commercialized.*
- Other methods



Commercial rotational cure meter (in cross-section).
Winkler et al., *Proc. Euro. PVSEC*, 3482–3485 (2012).



Backside indentation (in cross-section) for degree of cure assessment.

Mickiewicz, *Proc. ATLAS/NIST Work. PV Mats. Durability*, 2011.

Using a Primary to Calibrate a Secondary Method

- A *rapid test* is necessary for quality and process control.
- Results of quickest methods are *formulation- or resin-specific*.
- Quickest methods often work well only for a *certain range of G*.

Solution: use a precise primary method to calibrate a rapid secondary method.

- The primary method allows for interpretation of the secondary.
- Accurately perform the primary (reference) measurement occasionally per EVA formulation.
- A variety of specimens (sheet, module; unaged & aged) may be examined using the secondary method(s).
- The secondary and primary methods can be correlated against module qualification results or processing conditions (lamination).

Use of Gel Content as the Primary Method

- Gel content selected as *most practical* primary method.
- Gel content has a *longstanding legacy* of use with PV EVA.
- Method quantifies the *% insoluble cross-linked gel*.
- Method does quantify the gel structure, *e.g.*, # bonds/molecule.

SITE	SPECIMEN SIZE {g}	APPARATUS TYPE	SOLVENT	SOLVENT VOLUME {ml}	SOAK TIME {hr}	SOAK TEMPERATURE {°C}	DRY TIME {hr}	DRY TEMPERATURE {°C}
ISO 10147	0.2	flask/reflux condenser	xylene	200:1 by mass	8	140	3	90
ASTM D2765 (method A)	0.3	flask/reflux condenser	xylene	350g/500mL (immerse)	12	140	to constant weight	150
ASTM D2765 (method C)	0.5	jar in heated oil bath	xylene	100	24	110	16	100
Arkema	0.3	flask/reflux condenser	xylene	2000	12	140	4	150
Bridgestone			xylene	full	6	140	8	85
First PV	0.5	flask/reflux condenser	xylene	300	5	140	3	140
Mitsui	1	jar in heated oven	xylene	100	12	110	8	110
NREL	1	Soxhlet	toluene	100-120	24	130-140	24	23
Solutia	1.5	unspecified	xylene	90	8	140	12	90
Stevens Urethane	1	jar in heated oven	toluene	100	20	60	4	105
STR	1	jar in heated oven	toluene	100	20	60	4	105
Trina Solar	0.2	flask/reflux condenser		≥1000	5	138-143	3	150
<i>Proposed Standard</i>	1±0.5	Soxhlet	xylene	≥100	12	140±2.5	4	140±2.5

Results of survey of the EVA degree of cure standard group, relative to existing standards and IEC 62755 (proposed).

- The disparate solvents and tests conditions cannot improve the repeatability or reproducibility of the gel content test.

⇒ Let's standardize the method!

Details of a Standardized Gel-Content Test

Solvent: use *xylene* (mixed isomers, CAS 1330-20-7).

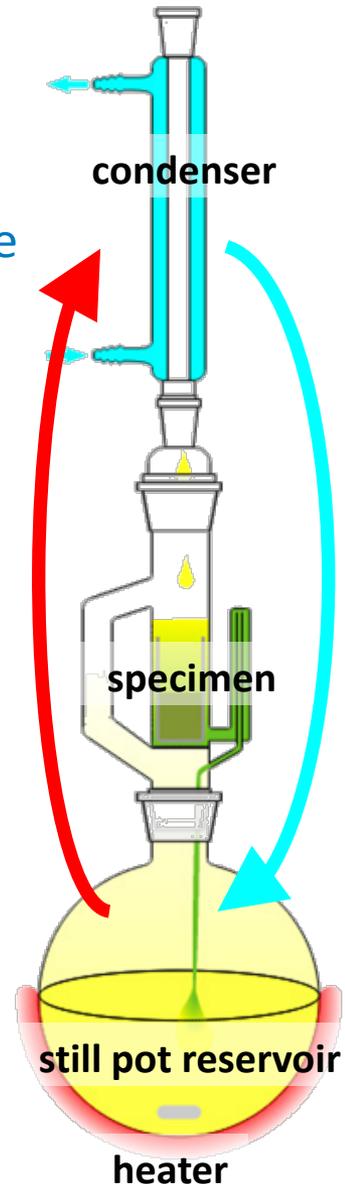
- Temperature of use, *e.g.*, boil at 140°C, cannot induce curing.
- *Condensed temperature* important relative to T_{melt} EVA.
- Use *antioxidant* additive, *e.g.*, 0.1% wt. BHT, in the solvent & thimble to *prevent decomposition* and *additional curing*.

Apparatus: use *soxhlet extractor*, with *porous membrane filter*.

- Closed system prevents contamination, solvent concentration effects, and improves solvent circulation.
- A pressure relief is recommended for safety.
- A fine filter thimble will retain undissolved EVA gel.
Do not use a wire cage as in ISO 10147 or ASTM D2765.

Additional Details: specimen mass, time, temperature in standard —standardized conditions for direct comparison between institutions.

- LONG DURATION test (12 + 4 hours)!



Schematic of a soxhlet extractor.

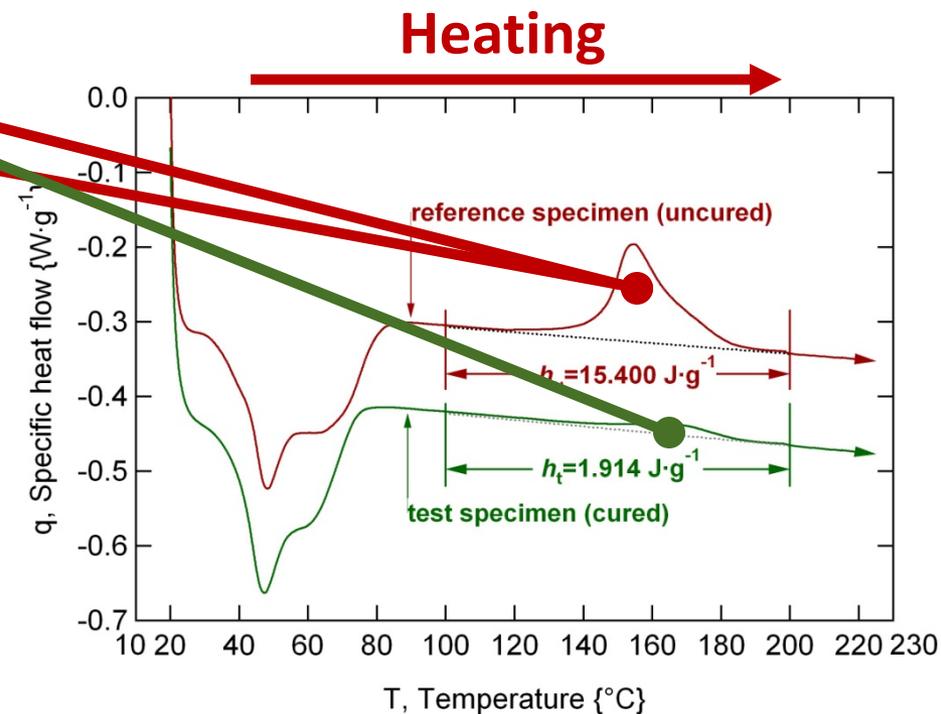
http://en.wikipedia.org/wiki/File:Soxhlet_extractor.svg

Details of the DSC Residual Enthalpy Test Method

- Exothermic peroxide reaction \Rightarrow measure enthalpy of reaction using DSC.
- Small sample size, 5–9 mg.
- Fast test time, $20^{\circ}\text{C} \rightarrow 225^{\circ}\text{C}$ at $10^{\circ}\text{C}\cdot\text{min}^{-1}$
- A single uncured reference specimen must be characterized in addition to the test specimen(s).

$$G_e = 100 \frac{(h_u - h_t)}{h_u}$$

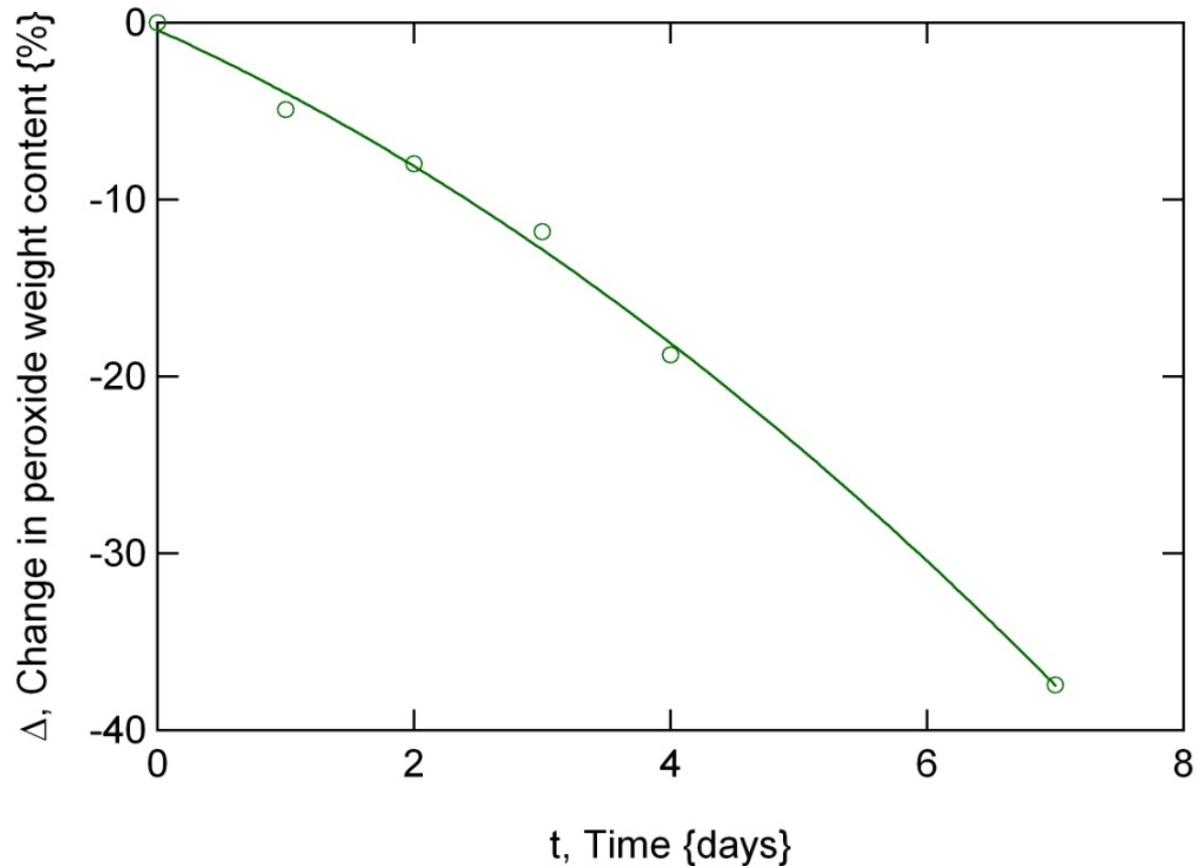
- Results depend on the EVA formulation, e.g., the type and concentration of peroxide.
- DSC can't be used to directly determine processing conditions (DSC furnace has different operating characteristics than a laminator \therefore test laminated specimens using DSC).



Heat flow for a partially cured test specimen and an uncured specimen composed of the same EVA.

Evaporation of Peroxide May Limit the DSC Enthalpy Test

- When properly stored EVA (peroxide) will remain fresh for ~6 months.



Measured weight change (via mass chromatography) of EVA sheet freely exposed to the ambient environment .

- Reactive peroxide chemistry will also decompose over time (months).
⇒ **Proper storage and prompt examination of G are necessary!**

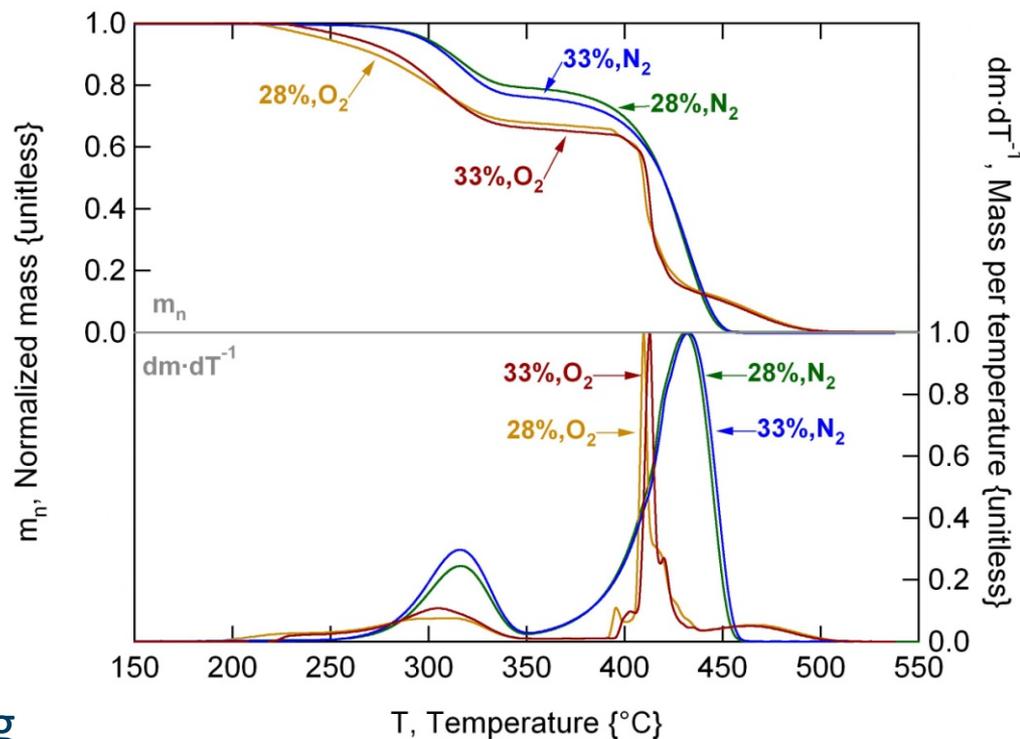
Thermal Decomposition of EVA May Limit the DSC Enthalpy Test

- Perform DSC residual enthalpy test well above cure temperature to ensure complete characterization.
- EVA will deacetylate (lose sidegroups) and depolymerize at high temperature.
- What maximum temperature should be used for DSC?

Modulated TGA used to quantify the decomposition of EVA:

- Additives can volatilize at temperatures $> 200^{\circ}\text{C}$.
- T_{max} [deacetylation] $\sim 310^{\circ}\text{C}$.
- T_{max} [depolymerization] $\sim 420^{\circ}\text{C}$.

\Rightarrow The standard recommends measuring to 225°C , but integrating the enthalpy up to 200°C .



Mass loss and its derivative with temperature for 28% and 33% VAc EVA in pure-N₂ or O₂-containing atmospheres.
See also summary table in appendix of this presentation.

Details of the DSC Melt/Freeze Method (1)

- T value and data profile at freeze transition vary with cross-linking.
- Depends on molecular structure, not peroxide concentration.
- Small sample size, 5–9 mg.
- Fast test time, $20^{\circ}\text{C} \rightarrow 100^{\circ}\text{C} \rightarrow -20^{\circ}\text{C}$ at $10^{\circ}\text{C}\cdot\text{min}^{-1}$
- Requires 1 uncured *and* 1 extensively cured reference specimen in addition to the test specimen(s).

$$G_c = \frac{T_{c,u} - T_{c,t}}{T_{c,u} - T_{c,m}} 100$$

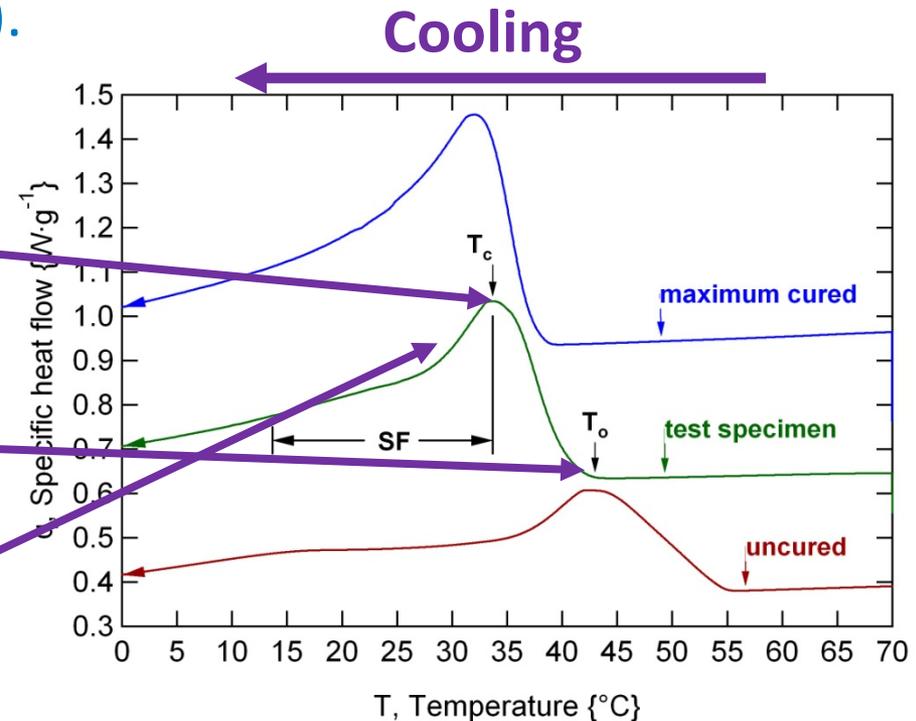
(Maximum) crystallization temperature

$$G_o = \frac{T_{o,u} - T_{o,t}}{T_{o,u} - T_{o,m}} 100$$

Crystallization onset temperature

$$G_{SF} = \frac{\%SF_{,u} - \%SF_{,t}}{\%SF_{,u} - \%SF_{,m}} 100$$

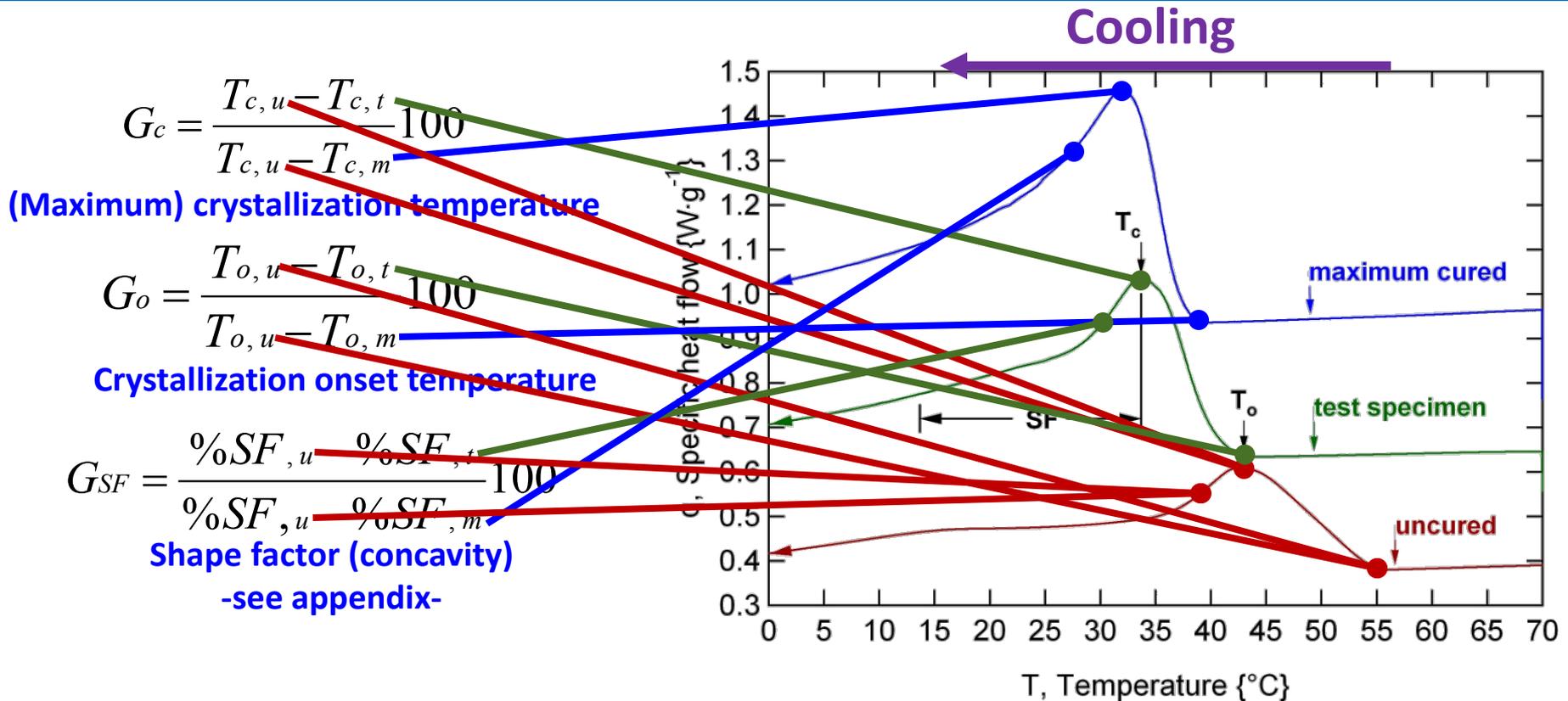
Shape factor (concavity)



Cooling profiles for an EVA test specimen, relative to samples with no thermal history (“uncured”) or extensively (“maximum”) cured.

- Degree of cure is the average of the three G parameters.

Details of the DSC Melt/Freeze Method (2)



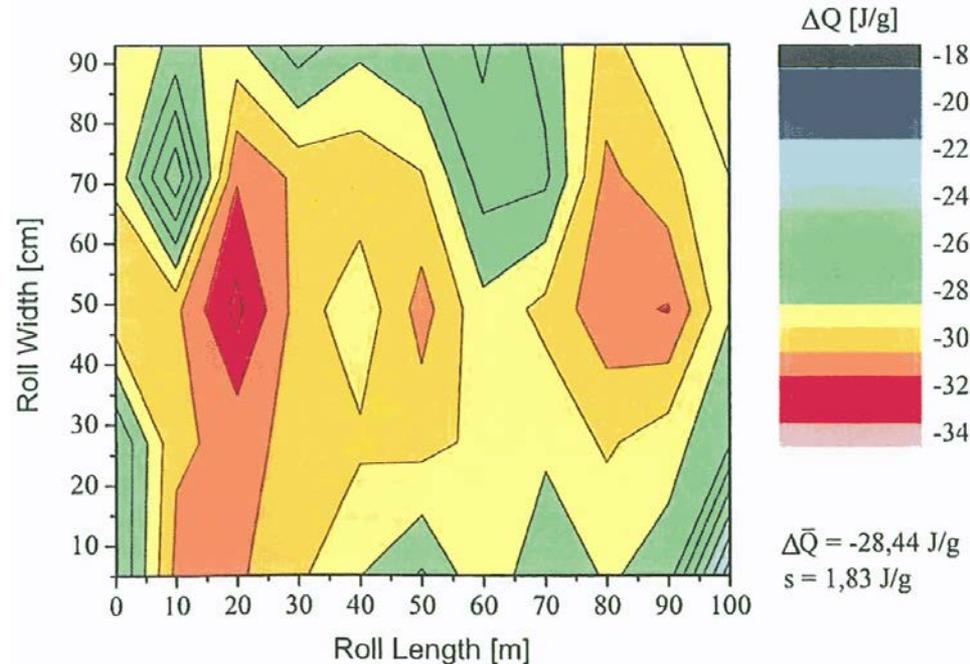
Limitations:

- Results subject to EVA resin, including vinyl acetate content, VAc.
- Results subject to the effect of aging, e.g., UV cross-linking.

Cooling profiles for an EVA test specimen, relative to samples with no thermal history (“uncured”) or extensively (“maximum”) cured.

Sample Volume and Heterogeneity of Peroxide in EVA May Limit Secondary (DSC) Test Results

- Small sample size in DSC allows heterogeneity in rolls to be mapped.



Enthalpy map, obtained from an EVA roll.

Schultze et al., *PV Intl*, 2011, 118–126.

- The uniformity of additives has not been rigorously studied.
- Enthalpy mapping may motivate better quality control.
- Additive heterogeneity may limit the repeatability & reproducibility of the secondary (DSC) test methods.

Details of a Round-Robin Experiment in Support of the EVA Degree of Cure Standard

Goals:

- Quantify repeatability & reproducibility of primary (gel content) & secondary (DSC) methods.
- Aid test development, *e.g.*, bounds of integration for DSC enthalpy.
- Provide additional understanding about the curing of EVA.

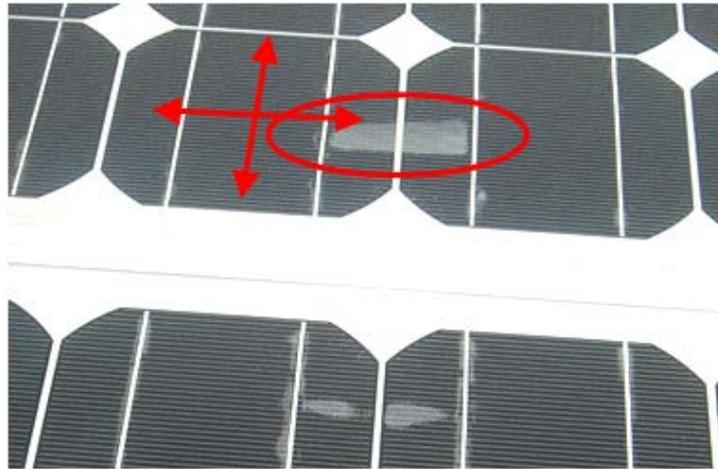
Key considerations:

- Follow *round-robin* guidelines in ASTM D7778 and ASTM E691.
- Examine both 28% and 33% VAc EVA.
- Examine EVA using different peroxides (type and concentration).
- Use additional methods, including: rotational cure meter; indentation; and modulated TGA, to gain insight about specimens examined.

Summary

- A degree of cure test for EVA, IEC 62755, is being developed within IEC TC82 WG2 to aid quality control.

Photo of undercured module, fielded for ~ 1 year. Problems can include *displaced components* and *delamination*.



- Gel content (solubility) test will be used as the “primary” method for calibration data that may be compared between institutions.
- DSC residual enthalpy and melt/freeze are “secondary” methods that may be used for more rapid quantification of degree of cure.

 We are looking for volunteers to support the standard development, including a round-robin test quantifying repeatability & reproducibility!
Contact David.Miller@nrel.gov

Acknowledgements

- NREL: Dr. Michael Kempe, Dr. Peter L. Hacke, Scott Deibert, Dylan Nobles

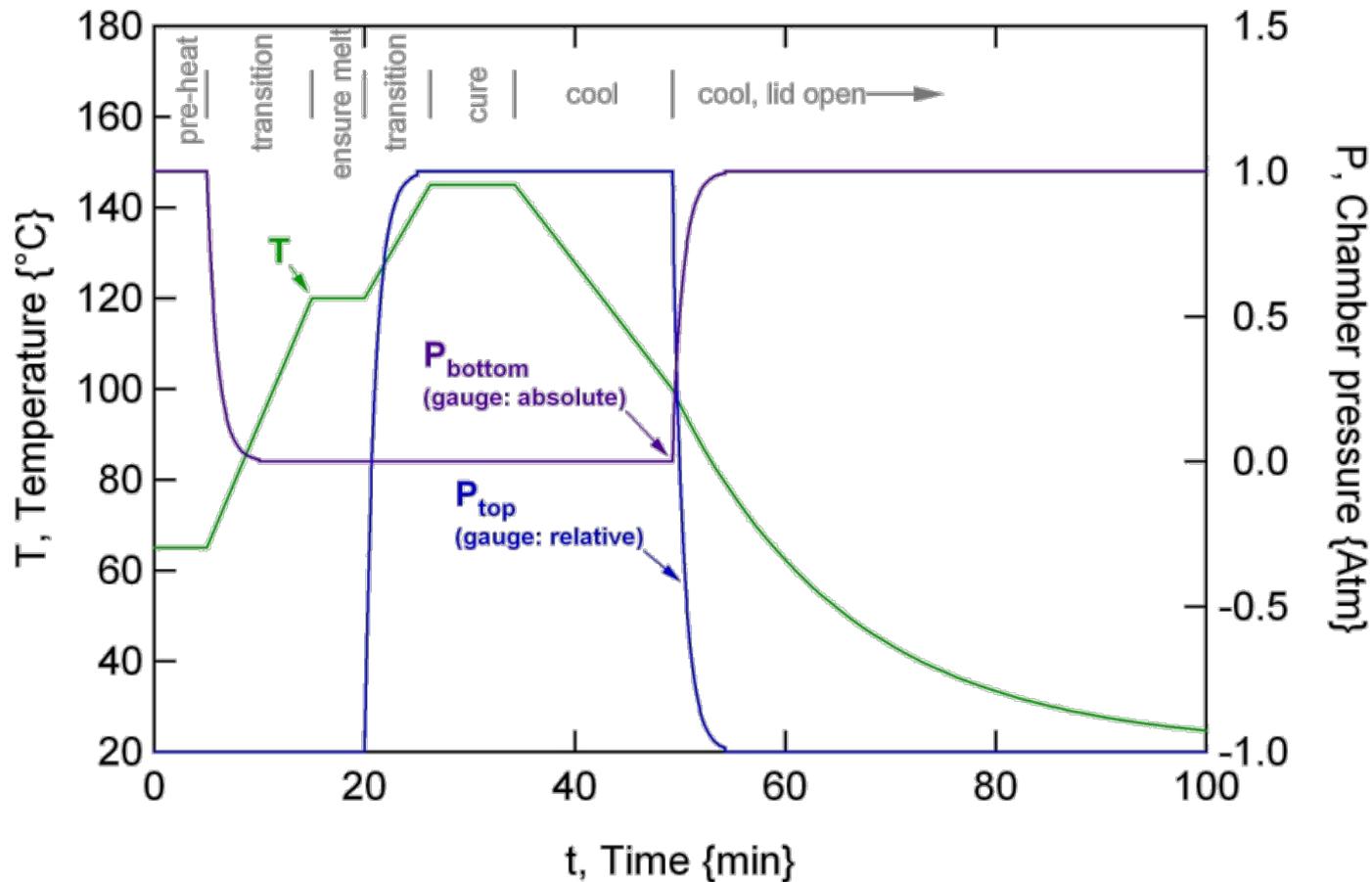
This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory.



NREL STM campus, Dennis Schroeder

See also the manuscript: “Examination of a Standardized Test for Evaluating the Degree of Cure of EVA Encapsulation,” Proc. Asian PVSEC 2013.

Appendix: Example Lamination Procedure



Temperature and pressure settings applied at NREL to *thoroughly cure* EVA for specimens in experiments. The lamination cycle is typically performed much faster in module manufacturing.

Appendix: Results of Modulated TGA

MATERIAL	MODEL	TEST	ATMOSPHERE	NOTE	T , 0.1% mass loss {°C}	T , 0.5% mass loss {°C}	T , 5% mass loss {°C}	T , 50% mass loss {°C}	T , Peak ₁ {°C}	T , Peak ₂ {°C}	T , Peak ₃ {°C}	FWHM {°C}	FREQUENCY FACTOR: $c_{1, avg}$ (s ⁻¹)	FREQUENCY FACTOR: $c_{1, st dev}$ (s ⁻¹)	$E_{a1, avg}$ (kJ/mol)	$E_{a1, st dev}$ (kJ/mol)	FWHM {°C}	FREQUENCY FACTOR: $c_{2, avg}$ (s ⁻¹)	FREQUENCY FACTOR: $c_{2, st dev}$ (s ⁻¹)	$E_{a2, avg}$ (kJ/mol)	$E_{a2, st dev}$ (kJ/mol)
EVA	28%VAc	ramp	O ₂	no residual material	246.2	256.2	309.2	438.3	354.4	439.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
EVA	28%VAc	ramp	N ₂	no residual material	248.9	295.1	343.1	466.4	365.2	479.8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
EVA	28%VAc	modulated	O ₂	no residual material	210.1	214.4	246.7	409.6	310.1	409.7	N/A	48.5	2.23E+10	1.11E-01	159.4	11.7	2.9	6.60E+15	9.69E+04	247.5	88.1
EVA	28%VAc	modulated	N ₂	no residual material	190.5	241.6	298.5	419.6	316.4	430.7	N/A	26.3	1.04E+13	5.10E-02	192.8	7.7	24.0	2.08E+12	3.54E-01	205.9	16.9
EVA	33%VAc	ramp	O ₂	residual grey char	252.3	264.1	317.5	442.9	354.7	443.2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
EVA	33%VAc	ramp	N ₂	no residual material	188.0	290.0	339.0	461.7	362.9	475.9	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
EVA	33%VAc	modulated	O ₂	residual black char	106.5	228.7	262.2	411.5	304.1	412.8	N/A	32.1	1.18E+11	1.67E-01	166.8	13.4	3.5	9.78E+13	1.59E+00	219.5	26.7
EVA	33%VAc	modulated	N ₂	no residual material	70.8	235.1	296.5	419.6	315.9	432.3	N/A	26.4	2.21E+12	4.09E-02	184.4	6.5	24.4	2.95E+12	1.76E-01	208.4	13.2

Table summarizing ramp experiment (20°C·min⁻¹) and modulated experiment (1°C·min⁻¹) for 28% and 33% VAc EVA in pure-N₂ or O₂-containing atmospheres.

Appendix: Example of Determining Shape Factor

- Calculate shape factor (SF) from inverse $[Q]$ and its convolution with T .
- Determine at max $[T \cdot Q^{-1}]$ and at $(T_c - 20^\circ\text{C})$.

$$SF = \frac{[T \cdot Q^{-1}]_{\max}}{T_c \cdot [Q^{-1}]_{T_c-20}} 100$$

- SF calculation can be automated.

Example showing the analysis, generating the data points for the SF computation.

The shape factor of 66.9% is determined for

$$T_{[T \cdot Q^{-1}]_{\max}} = 27.4^\circ\text{C}, Q^{-1}_{[T \cdot Q^{-1}]_{\max}} = 0.336 \text{ mW}^{-1},$$

$$T_c = 32.1^\circ\text{C}, \text{ and } Q^{-1}_{T_c-20} = 0.429 \text{ mW}^{-1}.$$

