Cure and Filler Analysis of Compression Mounting Media Alternatives

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Buehler Manufacturing is researching compression mounting materials that can cure faster than current media. The minimum temperature for sufficient cure was determined to be 160°C from visual inspection and differential scanning calorimetry tests. Shore D hardness tests were run to compare new filler types against the Buehler standard. A model to predict the time for the mount to reach cure temperature by calculating the thermal diffusivities of potential matrix/filler combinations in an unpressurized environment was developed using MATLAB. Based solely on thermal diffusivity, edge plane orientated graphite and carbon fibers allow the media to reach cure temperature faster but factors like filler anisotropy and aspect ratio also must be considered.

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Project Background

- Compression mounting allows small metal samples to be polished, etched, and viewed under a microscope for microstructure evaluation.
- Used in research and development and failure analysis in manufacturing industries.
- Polymer mounting powder melts or crosslinks its chains under pressure around a specimen.
- The goal of this project is to identify fast-curing mounting media.

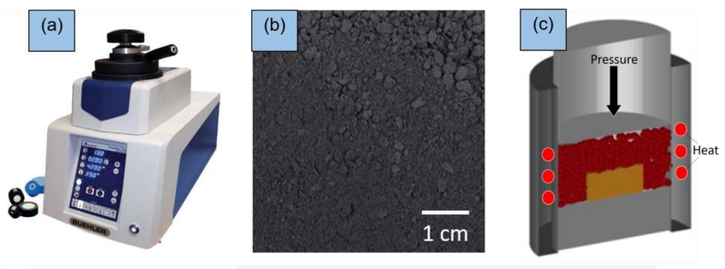


Figure 1: (a) Mounting press, (b) mount media, and (c) sketch of mounting press cross-section. [Adapted from Buehler]

Properties of interest to gain competitive market advantage

- Maximizing thermal diffusivity allows heat to flow through the material and heat the bulk polymer faster.
- Matching hardness to the metal specimen allows for smooth polishing that erodes both materials at similar rates.
- Maximizing cure takes more time in the mounting press but increases the mount stability. Partial curing to a stable point is ideal.

Experimental Procedure

- Compression mounting tests of Buehler branded phenolic resin and diallyl phthalate were conducted on the Buehler SimpliMet 4000 compression mounter.

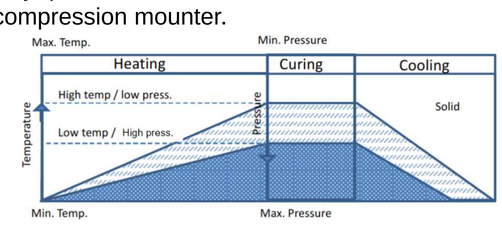


Figure 2: Graphs of qualitatively visualized heating cycles for compression mounting of thermoset resins. [Adapted from Buehler]

- Hardness was measured for each specimen using the Shore D method using a Phase II model No. PHT-980 durometer.
- Ethanol test - cure was quantified by monomer leaching using a method used by the industrial sponsor by submerging in 99% ethanol and measuring cross-sectional area surface discoloration.

$$\%\ cure = \frac{h - x}{x} \cdot 100\% \qquad (\boldsymbol{Eq.1})$$

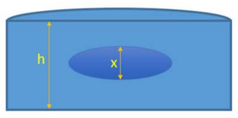


Figure 3: Schematic of specimen height (h) and cross-sectional surface discoloration (x) and equation for the Ethanol test **(Eq. 1)** [Adapted from Buehler].

- Dynamic and isothermal tests were conducted using differential scanning calorimetry (DSC) to determine when cure occurs by measuring heat released at a range of temperatures.

Model Development

Heat is uniformly transferred through the mount

$$\frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\alpha}{r^2}\left(\frac{\partial^2 T}{\partial \theta^2}\right) + \alpha\frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}}{\rho c_p} = \frac{\partial T}{\partial t} \qquad (\boldsymbol{Eq.2})$$

No vertical heating — No heat generation

Assuming: no heat loss, T_R is constant, there is perfect contact between all the elements, there are no changes in the properties or dimensions, no specimen mounted within media, the system begins at room temperature and stays at atmospheric pressure.

$$\frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = \frac{\partial T}{\partial t} \qquad (\boldsymbol{Eq.3})$$

- ***Eq. 3*** was solved w.r.t. to penetration depth and time (***Eq. 4***). This gives the amount of time necessary for the heat to reach the center of the mount without a temperature change (***Eq. 5***).

$$t = \frac{\delta^2}{12\alpha} - \frac{\delta^3}{36\alpha} \qquad (\boldsymbol{Eq.4}) \qquad t_{crit} = \frac{R^2}{18\alpha} \qquad (\boldsymbol{Eq.5})$$

- Knowing the critical time, ***Eq. 3*** was solved w.r.t. to temperature changes, position, and time (***Eq. 6***). This gives the final solution that shows how the heat moves through the mount after the critical time (***Eq. 7***).

$$\theta = \exp\left(\frac{-24}{5}\tau\right)\varepsilon^2 - 2\exp\left(\frac{-24}{5}\tau\right)\varepsilon + 1 \qquad (\boldsymbol{Eq.6})$$

$$\frac{T(r,t)-T_o}{T_R-T_o} = \exp\left(\frac{-24\alpha t}{5R^2} + \frac{4}{15}\right)\left(\frac{R-r}{R}\right)^2 - 2\exp\left(\frac{-24\alpha t}{5R^2} + \frac{4}{15}\right)\left(\frac{R-r}{R}\right) + 1 \qquad (\boldsymbol{Eq.7})$$

Variables:
t - time (seconds)
r - radius (meters) (R = 0.016m)
T – temperature (°C)
(T_o= 23°C, T_R = 180°C)
α - thermal diffusivity (m²/sec)
δ – heat penetration depth (m)
Non dimensional variables:

$$(\boldsymbol{Eq.8})\ \tau = \frac{\alpha}{R^2}(t - t_{crit})$$

$$(\boldsymbol{Eq.9})\ \varepsilon = \frac{R - r}{R}$$

$$(\boldsymbol{Eq.10})\ \theta = \frac{T_{cure} - T_0}{T_R - T_0}$$

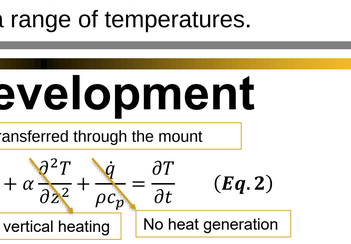


Figure 4: Sketch showing how variables in the model relate to the conditions within the mounting press

Results

Determining Percent Cure:

- Resins were mounted using recommended product parameters.
- Diallyl phthalate (DAP) specimens showed a decreasing cure % for both inspection method as peak temperature decreased.
- Absence of residue after leaching indicates a passing specimen.
- Similar trends are observed for the phenolic resins.

Table 1: Compression mounting parameters and determined cure from ethanol testing and isothermal DSC testing in **Figure 6** for DAP resin.

#	Inspection Method	Temperature [C°]	Pressure [bar]	Heating [min]	Cooling [min]	Cure [%]	Pass/Fail
1	Ethanol	180	290	1.5	2	76	Pass
2	Ethanol	160	290*	1.5	2	0	Fail
3	Ethanol	160	290	1.5	2	73	Pass
4	DSC	180	1	5	N/A	63**	N/A
5	DSC	140	1	7.5	N/A	34**	N/A

* Experienced sealing error during mounting run
** Cure % for DSC was calculated using $\Delta H_{DSC}/\Delta H_{reference}$ for a DAP equivalent (73 J/g).

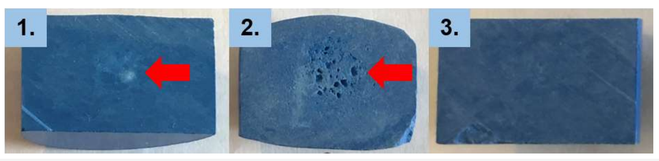


Figure 5: Cross-section photographs of DAP specimens #1, 2 and 3 after ethanol testing. Arrows indicate discoloration and/or pores in uncured regions. Each sample is 1.25 inches in diameter (0.0318 m).

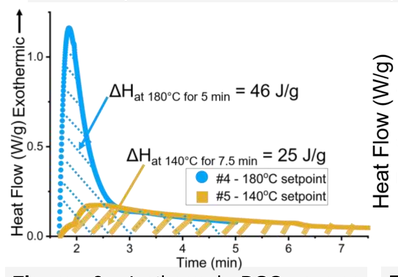


Figure 6: Isothermal DSC curves showing heat released as media is heated to 180°C (#4), and 140 °C (#5).

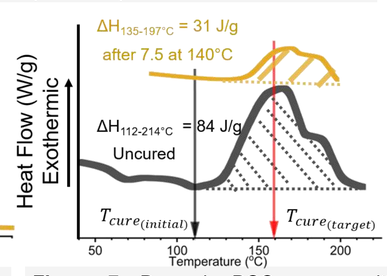
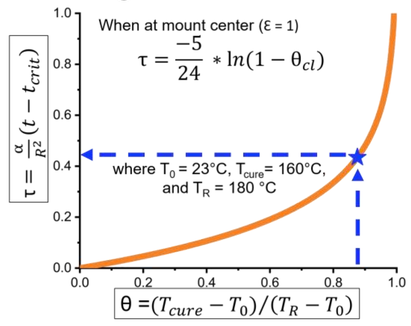


Figure 7: Dynamic DSC curves with ΔH_{rxn} for DAP at different cure levels. Initial and target cure values are marked.

Modeling Final Cure Time:



1. Calculate θ (temperature parameter).
2. Find τ (time parameter) from a modified ***(Eq. 6).***
3. Given R and α determine t using ***(Eq. 8)*** (when T reaches T_{cure} at the mount center).
4. Compare t_{final} for thermal diffusivities of different media compositions.

Figure 8: Plot relating the nondimensional parameters for temperature and time, at the center of the mount (ε=1). The blue arrows mark the conditions of our model (θ = 0.87, τ = 0.43).

Modeling Filler Performance:

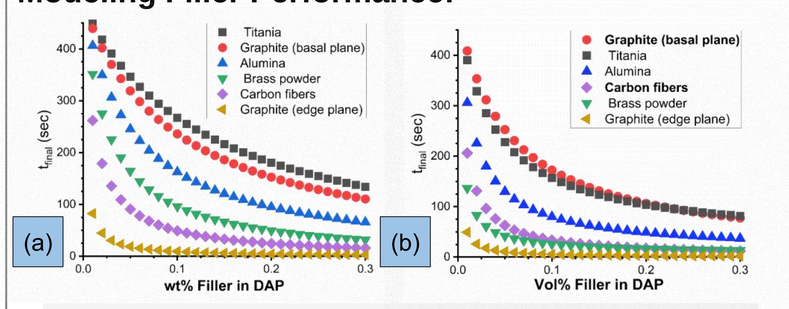


Figure 9: Plots showing effect of fillers on final time as a function of (a) weight %, how media composition is measured, and (b) volume %, which has greater effect on mechanical properties. T_R = 180°C and T_{cure} = 160 °C. Basal plane graphite and carbon fiber are bolded because their relative ranking shifted once measured in volume %.

Hardness Analysis:

Table 2: Table of mean hardness for filled PhenoCure mounts

Filler Composition	Hardness (Shore D)
No Filler	**81**
20 wt% Graphite	79
40 wt% Graphite	74
2 wt% Glass Fibers	80
10 wt% Brass	81
20 wt% Brass	82

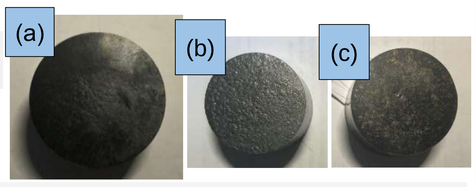


Figure 10: Pictures of mounts with different filler types in PhenoCure (a) no filler, (b) 20 wt% graphite, and (c) 10 wt% brass. Mount diameter is 1.25 in (0.0318 m).

- No significant change in hardness below 20 wt% for all tested fillers.

Discussion

Cure:

- % cure is better measured by ethanol testing because DSC can not replicate the pressure and heating rate conditions of the mounting press. (**Table 2**, **Figure 5 and 6**)
- Exothermic peak from DSC in **Figure 7** sets $T_{cure(target)}$ as minimum temp. for sufficient cure in model. (**Figure 11**)

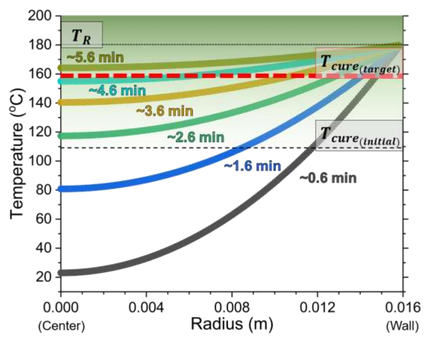


Figure 11: Model of temperature profile starting at t_{crit} with showing 1 min timesteps for a DAP equivalent where t_{final} ~ 5.1 min.

Model:

- **Figures 8, 9 and 11** are from a MATLAB tool that compares effectiveness of new media/filler compositions before experimental tests.
- A target Δt_{final} can also be set to see what change in diffusivity is required.

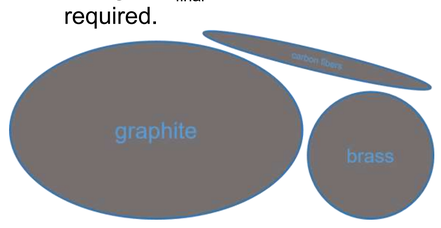


Figure 12: Diagram of relative particle sizes and aspect ratios for sample particles. Carbon fiber has the most ideal particle size and shape as a filler.

Particle Size:

- Particles with higher aspect ratio induce better heat transfer (i.e. carbon fiber).
- Smaller particles induce better heat transfer, to a lesser extent than aspect ratio.

Anisotropy in Fillers:

- In anisotropic materials, such as graphite and carbon fibers, the conductivity, and therefore diffusivity of materials is directionally dependent.
- Figure 9, shows two distinct lines for graphite that show the effect anisotropy can have on properties. The true values for a randomly-oriented graphite-filled mount exist in between these.
- It is important to note that other fillers, such as alumina and titania, can also display anisotropic behavior depending on how they were formed.

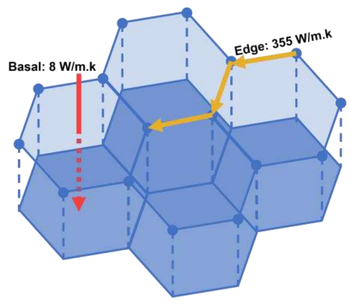


Figure 13: Sketch of the layered graphite structure. Heat can easily move through atomic bonds along the edge plane (gold) but must jump between layers grouped by Van der Waals forces along the basal plane (red).

Recommendations

- Target cure temperature for DAP and phenolic resins is 160°C.
- Utilize MATLAB model to compare t_{final} for experimental media.
- For fillers presented, 0-10 vol% filler shows largest decrease in time to reach T_{cure}.
- Edge plane graphite (2.34E-04 m²/s), carbon fibers (4.09E-05 m²/s) and brass powder (3.31E-05 m²/s) had highest thermal diffusivities of the fillers researched
- Buehler should investigate fillers with both high aspect ratios and directionality for improved thermal properties

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Additional sources used for mounting press model:

Acknowledgments

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MSE 430-440: Materials Processing and Design