Thermal Analysis and Modeling of Polymer and Filler Systems for Multiple Molding Processes

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Industrial Sponsors: Unnamed at Sponsor's Request

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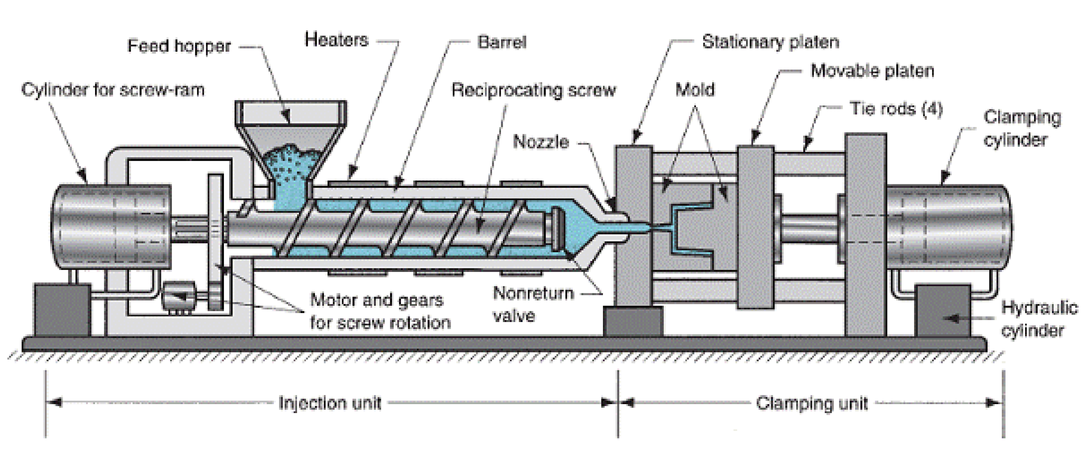
The project sponsor is looking for polymer-filler systems to decrease the cycle time in molding applications. A model that accounts for transient thermal conductivity as air leaves the system and the heat of polymerization was developed to predict the thermal behavior of polymer-filler systems without having to purchase materials and spend time on experiments. Additionally, the effect of preheating the polymer material before curing on the cure time was investigated. From the model, it can be determined incorporating as low as 1-2 vol% filler can drastically lower the time to reach the cure temperature. Further, preheating the polymer shortens the cure time of thermosets significantly.

This work is sponsored by **Unnamed Company** at sponsor's request.

Project Background

- Injection molded and compression molded components can benefit from the large economies of scale and complex shape across a wide range of industries and applications.
- Polymer fillers can affect both the thermal and mechanical properties of both thermoplastics and thermoset polymers.
- For this specific application, the Sponsor aims to identify a new polymer system that decrease the cycle time of their molding machine while maintaining similar mechanical and chemical performance to their current filled polymer products.



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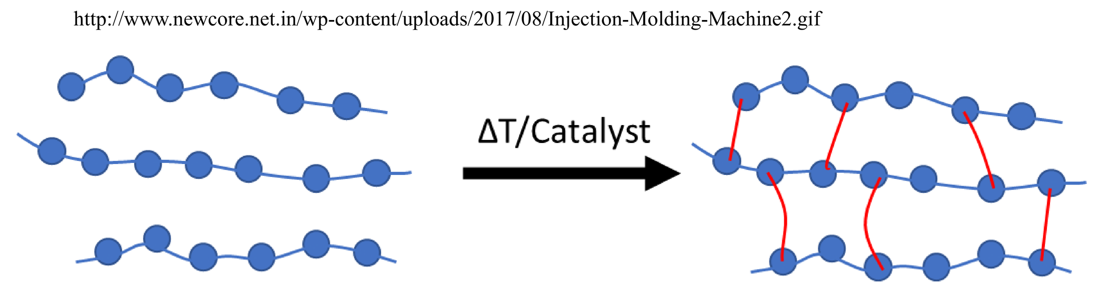

- Thermoset polymers are cured in molding through a chemical process called crosslinking. Increased temperature or the presence of a catalyst induces covalent bonds to form between monomers and their chains, creating a heavily bonded and durable sample.

Model Development

$$k\left[\frac{1}{r}\frac{d}{dr}\left(r\frac{dT}{dr}\right)+\frac{Q}{\rho c}\right]=\frac{dT}{dt}$$

- We used a MATLAB program for the heat transfer model while inputting constants specific to our system
- k = thermal conductivity, Q = heat generation from polymerization, r = radius, c = specific heat capacity, T = temperature, t = time, and ρ = density
- A transient function was coded into the program to continuously update the thermal conductivity as air leaves the system and heat generation from polymerization occurs
- Using differential scanning calorimetry (DSC), we investigated the amount of energy necessary to transform the polymer. We used this data to plot a change in area against temperature and create a line of best fit to address one of the experimental variables needed to make the model functional.

Experimental Procedure

- Heat flow experimentation were conducted using a Carver 3725 manual heated press and a custom mold with embedded thermocouples to record the thermal profile of multiple polymer and filler systems during the molding process.

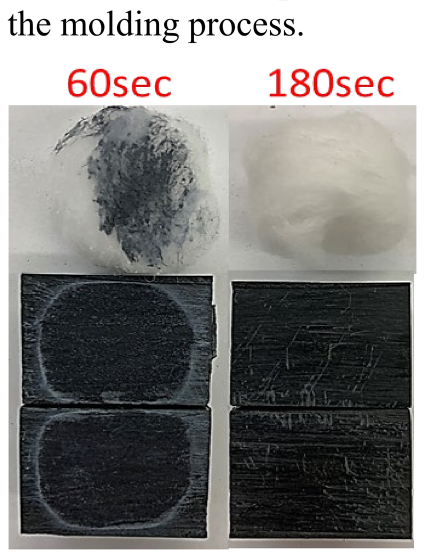

Figure 1: Difference in uncured (60sec) and cured (180sec) samples after ethanol testing.

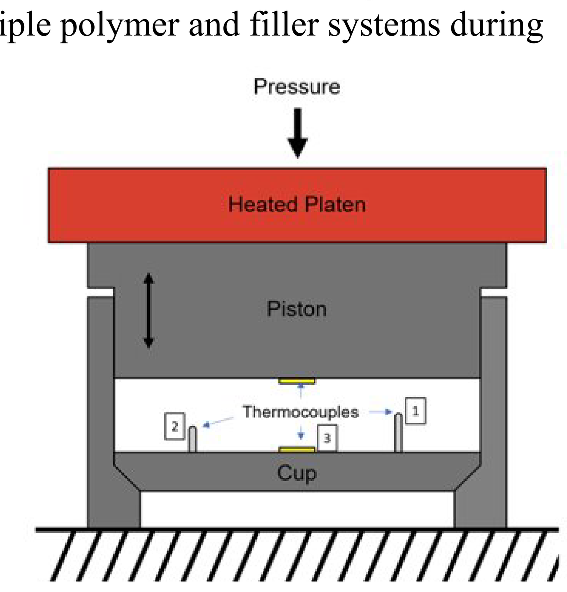

Figure 2: Mean rate of heating for different filler parameters in thermoset resin system.

- An array of thermoset polymer molded samples were created to find the borderline of complete cure, defined by lack of dissolved polymer on an ethanol-soaked sample. New samples were then preheated and molded at different heating times to observe how preheating can reduce the amount of time required for complete cure and were compared to non-preheated samples.

Experimental Results/Discussion

Table 1: Mean rate of heating for different filler parameters in thermoset resin system.

Filler	Thermal Conductivity ($\frac{\lambda_{Filler}}{\lambda_{Polymer}}$)	Vol. %	Shape Factor (SF)	Particle Size (µm)	Mean Rate of Heating (°C/sec)
Unfilled	1	-	-	-	0.11
A	413	**10**	1.0	300	0.12
A	416	**25**	1.0	300	0.18
B	962	10	**1.0**	44	0.25
B	962	10	**6.0**	35	0.48
C	215	10	1.3	**63**	0.19
C	215	10	1.3	**10.6**	0.23
C	215	10	1.3	**3.8**	0.18

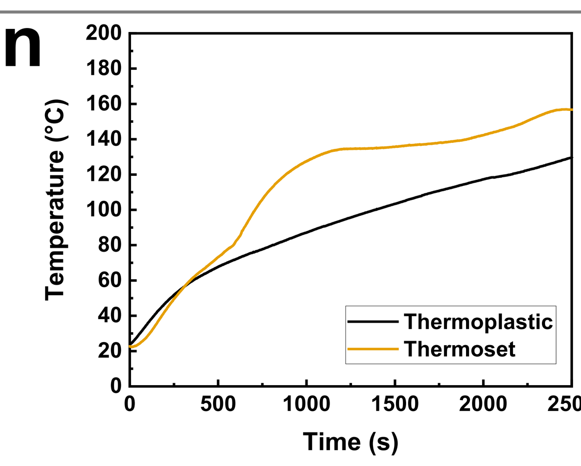

Figure 3: Mean thermal profile of thermoset and thermoplastic during heating cycle.

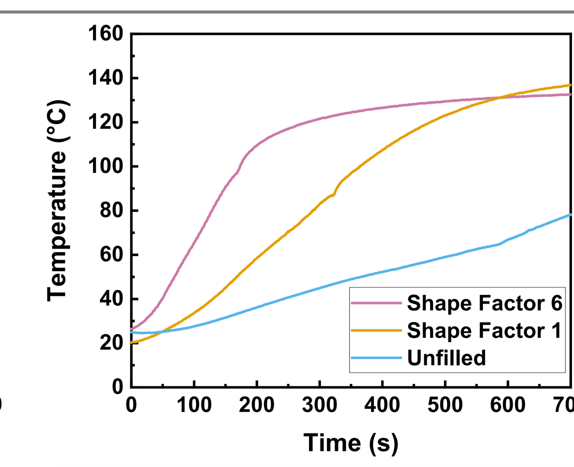

Figure 4: Mean thermal profile of 10 vol. % filler with different shape factor.

Filler Concentration

- Across all fillers in both experimental and modeled thermal behavior, increased filler volume saw an increased rate of heating seen in **Table 1**.
- Increased concentration permits more filler-filler contact leading to increased heat flow through the polymer system.

Particle Size

- Smaller particles leads to increased contact between both fillers and polymer.
- More surface contact leads to more opportunities for thermal interfacial resistance, decreasing overall thermal performance.[2]

Polymer Selection

- Lower heat capacity of thermoset led to a higher overall rate of heating than the thermoplastic, seen in **Figure 3**.
- Thermosets are limited by chemical kinetics as they cure and not only thermal kinetics like thermoplastics as seen in the dip within **Figure 3**.
- DSC analysis shows that much less energy is needed to initiate transformation for this thermoset (curing) than this thermoplastic (melting).

Filler Shape Factor

- High shape factor particles are able to better transport thermal energy as seen in **Table 1 and Figure 4** as well as modeled results.
- Increased surface area to volume ratio permits increased contact with surrounding polymer and filler
- Thermally anisotropic materials (Filler B), benefit more with a high shape factor.[1]

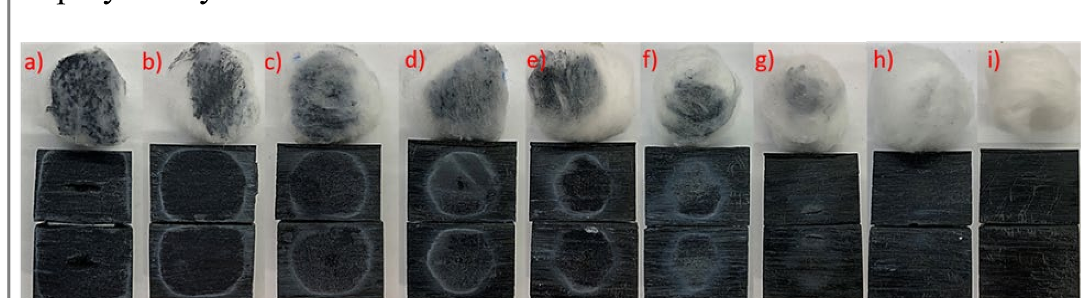

Figure 5: Shows cure of thermoset resin system as a function of heating time. Heating time from a) to i) 10 sec, 60 sec, 90 sec, 120 sec, 130 sec, 140 sec, 150 sec, 160 sec, 180 sec.

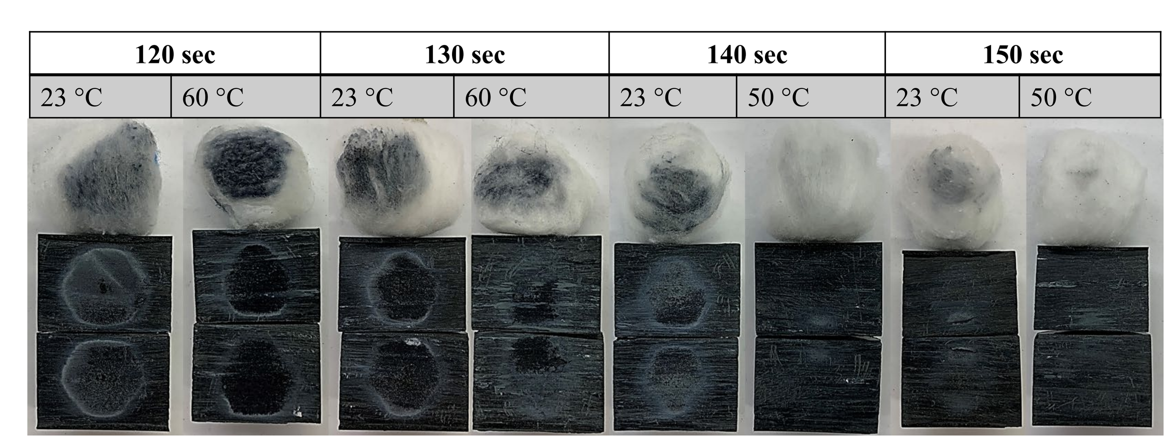

Figure 6: Shows cure as a function of preheating temperature and heating time. Heating time for each pair of samples displayed above each image pair. Images also contain temperature of polymer at start of molding. All mounts were the same mass of polymer.

- Preheat experimentation determined that preheating polymer before molding can have a significant impact on cure percentage. **Figure 6** demonstrates that when preheated to 50 °C samples mounted at 140 seconds are near completely cured, which is a 22 % reduction in cure percentage compared to the 180 seconds it takes when not preheated.

Model Results/Discussion

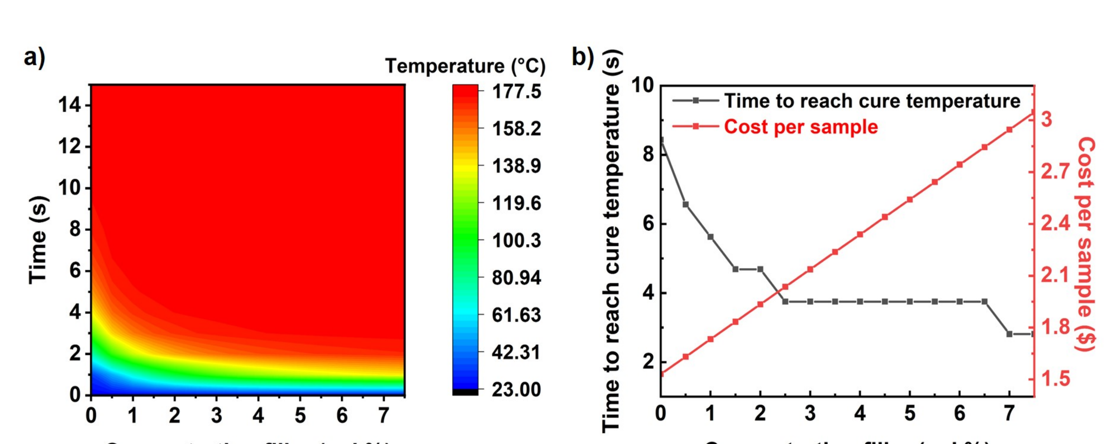

Figure 7: Plots of data output from model for filler C. a) colorimetric representation; b) line graph comparing rate of heat transfer and cost per sample for a range of filler concentrations

- The above plots show the options to represent data output from the model
- Part a shows a colorimetric representation of the temperature profile at the center point of the system over time for a range of filler concentrations
- Part b plots the time it takes the center point of the system to reach the cure temperature and compares to the cost per sample

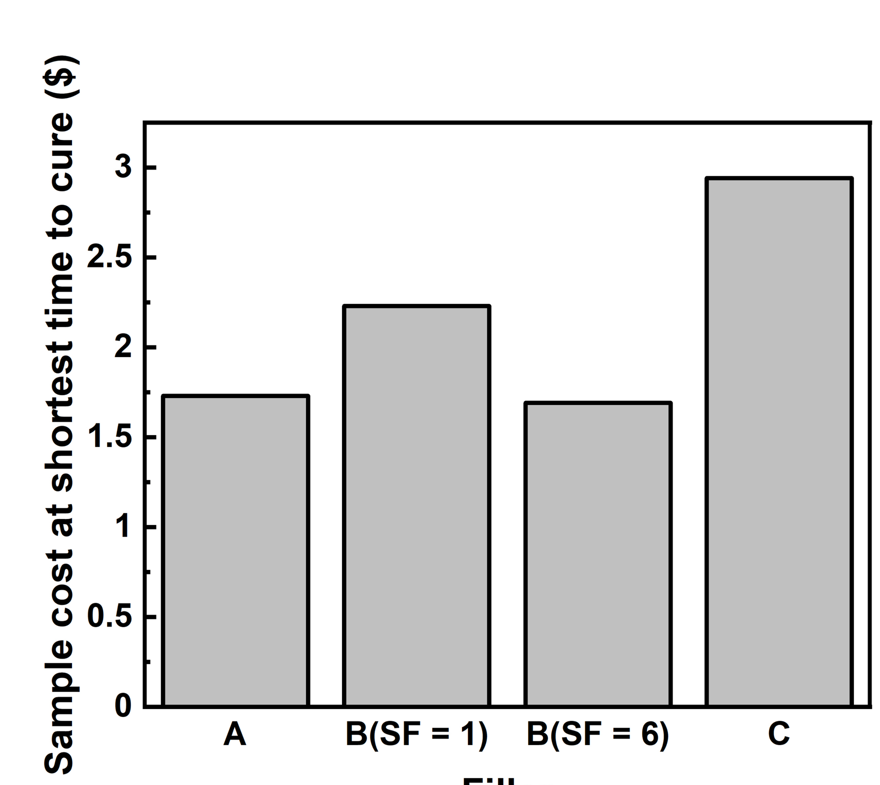

Figure 8: Bar graph representing the cost per sample for the minimum concentration of filler at the fastest heat rate for different filler options

Recommendations

- Leverage modeling tools to identify high preforming and cost-effective polymer systems.
- Utilize high shape factor anisotropic fillers to increase thermal performance.
- Investigate impact on mechanical and chemical properties of recommended filler combinations.
- Pre-heat thermoset polymer for high throughput applications.
- Further investigate long term effects of preheating on thermoset performance.

References

(1) Rivière, L.; Lonjon, A.; Dantras, E.; Lacabanne, C.; Olivier, P.; Gleizes, N. R. Macromolecular Nanotechnology Silver Fillers Aspect Ratio Influence on Electrical and Thermal Conductivity in PEEK/Ag Nanocomposites. **2016**. https://doi.org/10.1016/j.eurpolymj.2016.08.003.

(2) Boyard, N. 6.5.2 Interfacial Thermal Resistance. *Heat Transfer in Polymer Composite Materials - Forming Processes*. John Wiley & Sons 2016.