SAND2019-9986C

APO-BMI and the Two-tone Billet: A material investigation into polymorphism

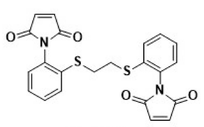
Adriana Pavia Sanders

Materials Chemistry (8344), Sandia National Laboratories, Livermore, California, United States

Abstract

APO-BMI glass syntactic foams have suffered from intermittent "two-tone" coloration issues for over a decade. Historically, this issue has been approached through a series of methodical manipulations of processing parameters with target billet density changes having the largest effect on two-tone manifestation. The darker regions display greater density than the lighter regions and are always found on the upper part of the billet (Figure 1). However, little is known regarding the root cause of this discoloration and its mitigation. Our approach focusses on the known polymorphic (capable of different molecular packing orders) nature of the monomeric chemical species used to produce this billet, namely (1,2-bis(2-aminophenylthiol)ethane) bismaleimide) or APO-BMI (Scheme 1).

Polymorphic species can be the result of different structural conformations or solvate/hydrate species and properties such as melting point, color, and density can be different for each species. It is hypothesized that it is the polymorphic behavior of APO-BMI that was the reason for the two-tone discoloration seen with manufactured billets. Analysis was performed on the different APO-BMI polymorphs through differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). Three polymorphic species have been identified, including a previously unidentified hydrate. Through characterization and better understanding of these polymorphs, we have successfully achieved a single-tone billet under the same manufacturing conditions employed so far in which only two-tone samples have been previously observed.



Scheme 1. Molecular structure of APO-BMI

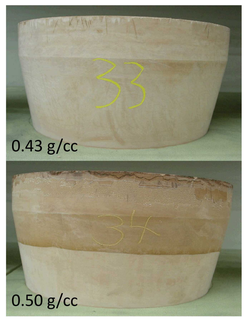
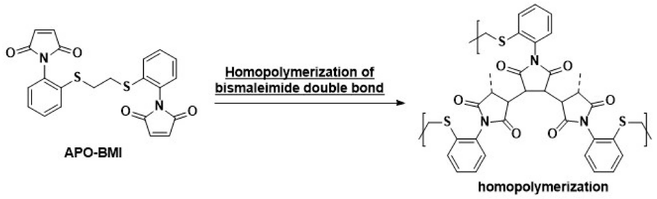


Figure 1. Billets at 0.43 g/cc (top) and 0.5 g/cc (bottom) showing two-tone phenomenon

Background Information: APO-BMI

APO-BMI (1, 2-bis(2-aminophenylthiol)ethane) bis-maleimide
Use to make syntactic foams (glass and carbon filled)
Historically has been noted to have a low melting point (T_m) of 110-120 °C
Undergoes thermal self-polymerization to crosslinked network
Produced at Production Agency site



Scheme 2. Self crosslinking reaction of APO-BMI

The monomer of interest, commonly referred to as APO-BMI, is a bismaleimide compound synthesized from the parent diamine 1,2-bis(2-aminophenylthio)ethane, also known as APO Cure 601. APO Cure 601 was originally identified as a potential replacement material to alleviate a need following health concerns regarding two commonly used monomers, methylenedianiline (MDA) and 4,4'-methylenebis(2-chloroaniline) (MOCA). APO-BMI and its parent diamine (not available commercially) are synthesized at the Production Agency site. APO-BMI undergoes self-crosslinking through an addition reaction at elevated temperatures (over 210 °C) to afford a highly crosslinked network (Scheme 2). It must be noted that impurities, most notably its parent diamine, are not completely removed from the product and can lead to side reactions such as Michael addition.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

DSC and APO-BMI Polymorphism

Historically, it has been noted that the melting temperature (T_m) of this material is low, ca. 120 °C, compared to other bis-maleimide compounds, 150 – 250 °C (Figure 2). It must be noted that as far back as 1986, there has been some controversy regarding the T_m of APO-BMI with some reports listing it closer to 140 °C. Throughout the years, the material has been identified to be a polymorph as supported by basic characterization performed at the production site and Los Alamos National Laboratory (LANL). Also, the specification for APO-BMI calls for two melting transitions, with the main T_m between 107-130 °C listed as primary and noting that material comprised of less than 65% of this lower T_m is unacceptable and should be discarded. Figure 3 displays a representative DSC of what would be considered an acceptable batch. As per the material specification, the primary transition would be integrated from 80 – 130 °C and the secondary transition from 135 – 145 °C.

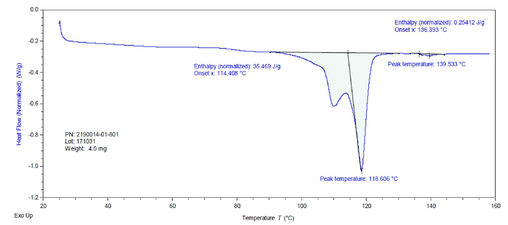


Figure 2. DSC characterization of APO-BMI showing T_m (°C)

Polymorphs can exist in more than one crystal structure (*e.g.* diamond and graphite) which can lead to differences in properties:

- Color
- Density
- Melting temperature
- Solubility
- Flow behavior

Two-tone overview

This issue was first noted for materials with nominal densities of 0.5 g/cc. Discoloration was accompanied by a density gradient across the billet from top to bottom with the higher density, and darker color, always appearing at the top of the billet (Figure 1). Initially, this coloration and density issue was attributed to process changes in production wherein several variable changes were implemented to resolution. Attempts to mitigate the issue included altering hold times prior to pressing the mold shut, mold temperatures, and mold loading techniques. No correlation between nominal density and the appearance of two-tone emerged. Nominal loading densities of lower than 0.45 g/cc effectively reduced or eliminated the two-tone coloration and its associated density gradient (Figure 3). Though this resolution of lowering the billet density worked, two-tone continued to be an issue that appeared sporadically within the desired density range with no apparent cause. It must also be mentioned that though two-tone does not immediately correlate with loss of mechanical strength required, some two-tone billets have failed to meet mechanical strength specification.

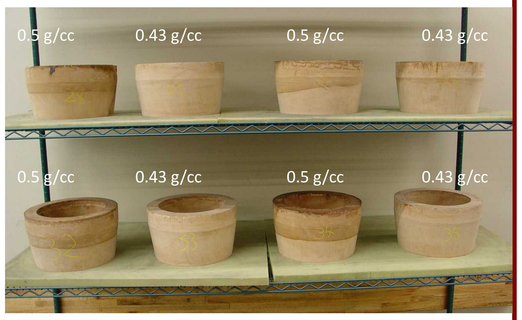


Figure 3. Alternating billets at 0.43 g/cc and 0.5 g/nominal densities demonstrating the ability to turn two-tone on and off

Current Approach: Two-tone as a Material Issue

After a comprehensive examination of historical experiments and data, it was determined that the discoloration and associated density gradient was likely a material issue associated with the polymorphic behavior of APO-BMI. Several material batches were obtained from production to probe this issue (Table 1).

Batch Number	Notes
070328	"Bad batch" falling out of compliance with spec due to high presence of high melt
090914	Nicknamed "magic batch" since no two-tone parts were ever obtained at nominal density
171031	Was noted to have high water content
180725	At the time currently in use for forward support production
181204	Next up for forward support production

Table 1. APO-BMI batches obtained by KCNSC

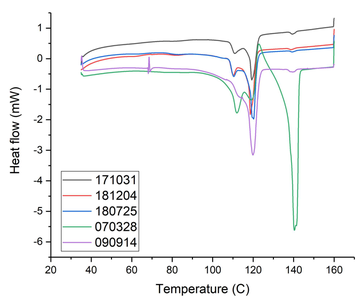


Figure 4. DSC characterization of all batches for comparative purposes. Data are not normalized.

DSC analysis was performed on all obtained batches (Figure 4). Special attention was afforded to differences between batch 090914 and all other batches. 090914 (purple) was nicknamed "magic batch" in the late 2000s since a two-tone billet was never produced at desired nominal densities (~0.43 – 0.45 g/cc) using this batch. Batches 180725 and 181204 (blue and red, respectively) are of immediate interest since they are currently scheduled to be used for the manufacturing of forward support billets. Batch 070328 (green) was requested since this batch falls out of specification due to the larger presence of high melt. Immediately a difference was noticed: a shoulder within the major thermal band centered at 110 °C is scientifically less pronounced in the magic batch than the rest of the batches. Although APO-BMI has previously been identified as a polymorph with former efforts distinguishing a low melt (generally located around 120 °C) and a high melt (around 140 °C) polymorphs, this shoulder has remained unidentified and disregarded. It was hypothesized that this should could represent the existence of a hydrate or solvated species of APO-BMI. Table 2 outlines two know facts alongside a hypothesized reasoning explained by the hydrate/solvate hypothesis.

Fact	Hypothesis
Two-tone coloration (darker) always observed at top of billet	Top is more loosely packed and more readily available for possible solvent evaporation
Darker tone samples display greater density than lighter tones	Evaporation of solvent/water has been shown to collapse conformational structure of polymorphs. This could lead to tighter molecular packing

Table 2. Hypothesizing over hydrate/solvate species on observed behaviors or two-tone billets

Searching for a Hydrate/Solvate

To probe the hydrate/solvate hypothesis, KCNSC was asked to increase the holding temperature of the billet from a few minutes to two hours at 153.7 °C. as observed in Figure 5, this appeared to drive the two-tone barrier further down the billet (experimental billet was ran at 0.45 g/cc nominal density). With this promising result, the hold time was increased to 24 h (Figure 6). What appeared to look like vent holes at the top of the billet were observed.

Figure 5. Billet following a two-hour hold at 153.7 °C

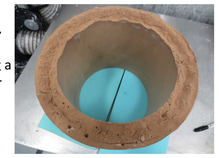


Figure 6. Billet following a 24-hour hold at 153.7 °C

It was deemed necessary to isolate and characterize the three identified polymorphs of APO-BMI. The high melt polymorph was isolated by heating a predominantly high melt batch (070328) at elevated temperatures until only high melt was observed through DSC (Figure 7). A color change was noted with increasing thermal treatment. TGA of the heated samples was also taken. Figure 8 shows a zoomed-in view of the TGA trace indicating a weight loss at *ca*. 100 °C which is indicative of loss of water, narrowing down the hypothesis to the existence of a hydrated species.

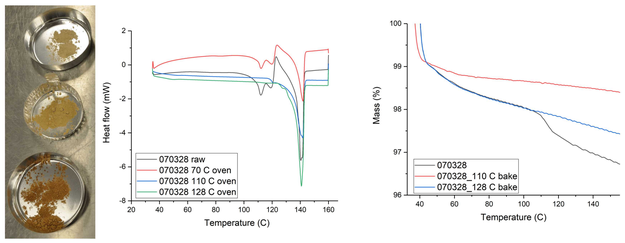


Figure 7. Samples of 070328 (left) heat treated at 70, 110, and 128 °C in descending order from top to bottom and their associated DSC traces.

Figure 8. TGA of heat treated 070328 samples showing the loss of water *at ca*. 100 °C

The low melt and hydrate materials were isolated by reprecipitation of the APO-BMI in water (from dimethylformamide). The hydrate was not isolated but obtained following a nitrogen purge of the drying material. The low melt was obtained by drying the wet material using hexanes as an azeotrope to promote the full removal of water. The DSC traces of the resulting materials can be seen in Figure 9 with the newly adopted nomenclature for the polymorphs where alpha refers to the high melt material, beta to the low melt, and hydrate to the non-fully isolated hydrate of APO-BMI.

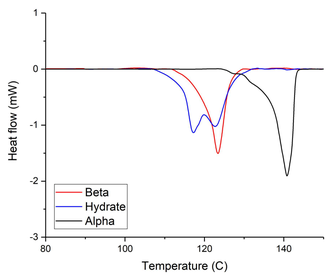


Figure 9. DSC of the three identified polymorphic species of APO-BMI

The solution: Single-tone Billet

Figure 10. First known single-tone billet at a nominal density of 0.5 g/cc

With the presented information at hand, a pretreatment recommendations was proposed to the production agency as a means of removing the hydrate to test if its presence could be the cause of the two-tone discoloration. The materials was treated at 71 °C in a vacuum over (based on lab-scale experimentation) and a billet was made at nominally 0.5 g/cc. The higher density was chosen to drive towards a two-tone billet with the goal of obtaining a single-tone billet (Figure 10.)