Evaluation of an Environmentally Friendly Plasticizer For Polyvinyl Butyral For Use in Tape Casting

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Abstract: An environmentally friendly plasticizer for polyvinyl butyral has been evaluated and compared with the industry standard – butyl benzyl phthalate. Properties such as the effect on the glass transition temperature of polyvinyl butyral and its compatibility with several grades of polyvinyl butyral are discussed. A direct comparison of this plasticizer is made with the industry standard in side-by-side tape casting runs.

Introduction: The object of this investigation was to evaluate a more environmentally friendly plasticizer for use with polyvinyl butyral in tape casting formulations. The new plasticizer, triethylene glycol di-2-ethylhexanoate (S-2075), was compared directly with one of the most common plasticizers used in tape casting, butyl benzyl phthalate.

The paper is divided into two sections, one relating to the environmental and health comparisons between the S-2075 plasticizer and the butyl benzyl phthalate plasticizer and the direct comparison of their effects as additives to the polyvinyl butyral binder and the second which relates to a direct comparison of tape formulations using the two different plasticizers.

The comparisons made included: the effect of each plasticizer on the T_g, glass transition temperature, and the compatibility level for each of the most common grades of polyvinyl butyral, including Butvar® brands B-76, B-79, B-90, and B-98. The tape casting formulation comparisons included the following: slip viscosity, green bulk density (GBD), green oxide only density (GOOD), green tape thickness, tape drying characteristics, green tape character including flexibility and tackiness, and sintered properties such as fired bulk density (FBD) and shrinkage.

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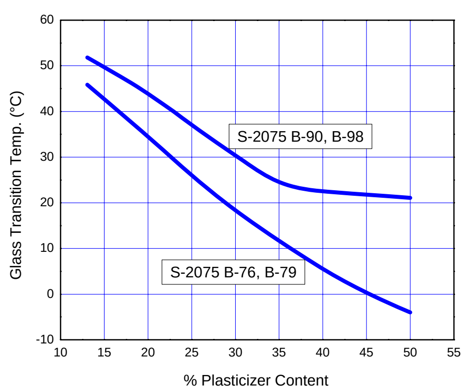
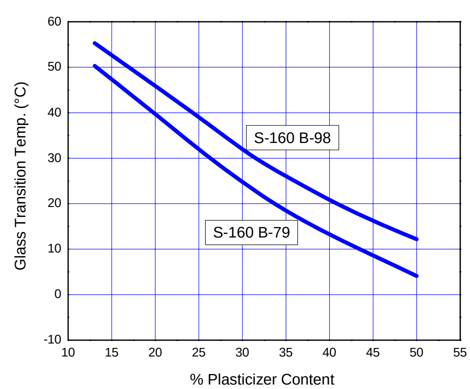
Part 1 - Plasticizer Comparisons:

Environmental and Health Considerations: Butyl benzyl phthalate (BBP), commercially sold as Santicizer® 160, has two environmental and health issues: 1) reproduction toxicity and 2) dangerous for the environment. These issues impact mainly Europe, but spread in particular into Asia as producers there are becoming more and more concerned about imports into Europe. Specifically, BBP is classified according to its MSDS as "toxic to reproduction" Category 2 which is to be considered as toxic to reproduction to man. Another widely used phthalate plasticizer for tape casting, diethylhexyl phthalate (commonly called dioctyl phthalate), is also a Category 2 reprotoxic chemical. Phthalates, including BBP, are expected to be included on the "dangerous substances" or "substances to be avoided" industry chemical lists. BBP is also considered as very toxic to aquatic life and has a potential to bio-accumulate. This has less of an impact, but it compares poorly against S-2075 plasticizer. The data for S-2075 show that it is not toxic to aquatic life (LC50 and EC50) > 97 mg/l) and that it is biodegradable. Therefore, based on the currently available data, S-2075 has a better profile than BBP and other phthalate plasticizers.

Plasticizer Effects on Polyvinyl Butyral:

Effect of Plasticizer Content on Tg
(Butvar® with Solutia S-2075 or Santicizer® 160 Plasticizer)





The glass transition temperature (Tg) profiles were determined by Dynamic Mechanical Analysis (DMA) with premixed Butvar® and plasticizer samples pressed into sheets. B-76 and B79 are 11-13% hydroxyl grades of PVB. B-90 and B-98 are 18-20% hydroxyl grades. The hydroxyl levels are expressed as weight percent polyvinyl alcohol.

The glass transition temperature (T_g) curves were determined by dynamic mechanical analysis (DMA) at a frequency of 1 Hz. Several glass transition measurements covering the plasticizer content range for each plotted curve were obtained. Samples of PVB and plasticizer were well-mixed in a Brabender Model D-51T and pressed into 0.040 inch thick sheets prior to T_g measurements.

During DMA testing, a material is subjected to a sinusoidal strain at a fixed frequency resulting in a sinusoidal stress which is at the same frequency but is out of phase with the applied strain. From this the complex modulus (E*) and the phase angle (δ) can be measured. The in-phase and out-of phase components of E* represent the Storage Modulus (E') and Loss Modulus (E''), respectively. The damping or dissipation factor (tan δ) is the ratio of the loss and storage moduli.

DMA is generally conducted over a wide temperature range in order to determine changes in E', E'' and tan δ. The primary glass-rubber transition (T_g) is characterized by a large decrease in E' and a maximum in both the E'' and Tan δ curves. The primary transition occurs in the amorphous regions of the polymer with the initiation of cooperative micro-Brownian motion of the molecular chains. The value of tan delta is sensitive to molecular mobility and is commonly used to determine the values of transition temperature in polymers.

The glass transition temperatures of PVB's containing a wide range of each plasticizer were determined using a Rheometrics Solids Analyzer (RSA-II) at a frequency of 1 Hz and a heating rate of 3°C/minute. Increasing plasticizer level is expected to result in a decrease in T_g. By plotting the T_g of each blend as a function of plasticizer level the level at which no further decrease in T_g can be determined. This level is taken to indicate the point at which the polymer can no longer take up any additional plasticizer.

Solutia S-2075 is found to have better compatibility and efficiency as measured by glass transition temperature than traditional Santicizer® S-160 butyl benzyl phthalate as well as other phthalate plasticizers, such as dioctyl phthalate evaluated in subsequent work, up to approximately 40% plasticizer content for 18-20% hydroxyl containing PVB. Up to 40% plasticizer content in PVB is more than sufficient to achieve a normal ambient temperature plasticization of 25°C. Solutia S-2075 is even more efficient than phthalate plasticizers, such as S-160 with low hydroxyl 10-13% type PVB, at all levels. S-2075 therefore can be used in lower concentrations to plasticize ceramic tapes.

Part 2 - Tape Casting Formulation Comparisons:

Experimental Procedure: Two tape casting batches were prepared with everything exactly the same with the exception of the primary plasticizer. The ceramic batch which was selected for the comparison was a 94% aluminum oxide formulation which is commonly utilized in thick film or multilayered ceramic packages. The formulation for the control batch was as follows:

Part 1:

Aluminum Oxide [1]	54.70 weight %
Clay [2]	1.19 weight %
Talc [3]	3.57 weight %
Fish Oil [4]	1.19 weight %
Xylenes [5]	12.74 weight %
Ethyl Alcohol, 95% [6]	12.74 weight %

Part 2:

Butyl Benzyl Phthalate [7]	4.55 weight %
Polyalkylene Glycol [8]	4.55 weight %
Polyvinyl Butyral [9]	4.76 weight %

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Part 2:

Triethylene Glycol Di-2-Ethylhexanoatel [10]	4.55 weight %
Polyalkylene Glycol [8]	4.55 weight %
Polyvinyl Butyral [9]	4.76 weight %

The fish oil is a dispersant for the inorganic components. The butyl benzyl phthalate and triethylene glycol di-2-ethylhexanoate are considered Type I plasticizers for the polyvinyl butyral and the polyalkylene glycol is a Type II plasticizer for the tape. The polyvinyl butyral is the binder for the system and it provides the strength and backbone for the tape.

The procedure followed for each batch was identical and was as follows:

1. Add 2 Kg of 1 inch U.S. Stoneware Burundum 96% alumina grinding media to a size 1 Roalox mill jar. This is about 1/3 capacity.
2. Dissolve the fish oil in the xylenes and add to the mill jar.
3. Add the ethyl alcohol to the mill jar.
4. Add the powders to the mill jar; the alumina was dried at > 100^0 C for 24 hours.
5. Dispersion mill at about 56 RPM for 24 hours on a jar roller.
6. Weigh and add the plasticizers to the mill jar.
7. Add the binder to the mill jar, stirring by hand to wet and mix the binder.
8. Mix for an additional 24 hours at about 56 RPM.
9. Pour the slip into HDPE containers.
10. Vacuum de-air for 8 minutes at 25 inches of Hg.
11. Measure the viscosity and temperature of the slip.

At this point the batches were ready for tape casting using the following casting parameters:

1. Blade Gap, two casts one at 0.030" and one at 0.050".
2. Ten (10) inch wide single doctor blade.
1. Carrier: Silicone Coated Mylar [11], 12 inch wide x 0.003 inch thick.
2. Casting Speed: 20 inches per minute.
3. Air flow on lowest setting with no heat.
4. No underbed heating.

After drying the following measurements were made on the green tape:

1. Thickness.
2. Green Bulk Density

Samples for sintering were punched from the control and experimental tapes. The punched pieces, which were 1" x 1.5", had the long axis oriented in the casting direction and the short axis oriented in the cross-casting direction. This provided a good basis for comparison of the shrinkage during sintering in the casting direction and in the cross casting direction.

Two samples from each casting run were sintered in an electric furnace in an ambient air atmosphere. The samples were sandwiched between two porous alumina cover plates during sintering to prevent warping and to maintain flatness.

The temperature/time schedule for the sintering was as follows:

RT to 500^{o} C @ 3^{o}C per minute
500^{o}C to 650^{o}C @ 1^{o}C per minute
Hold at 650^{o}C for 0.5 hour
650^{o}C to 1450^{o}C @ 5^{o}C per minute
1450^{o}C to 1500^{o}C @ 1^{o}C per minute
Hold at 1500^{o}C for 2 hours
Furnace Cool to RT

After sintering the samples were measured to determine the sintering shrinkage in the X, Y, and Z directions. Fired bulk density measurements were made using the Archimedes method by immersion in toluene.

Results and Discussion: The viscosity measurements on the ready to cast slips were made using an RV-4 spindle at 20 RPM using a Brookfield Viscometer. The measurements were as follows:

Control Batch	4750 cP	at	23.5^{o} C
	4500 cP	at	25.8^{o} C
Experimental Batch	3650 cP	at	27.4^{o} C

There were two measurements made on the control batch since the slip was divided into two portions for casting at two different doctor blade gap settings performed at different times during the day. As the room temperature increased the viscosity decreased as expected. There was only one measurement made for the experimental batch since only one cast was made with an adjustment of the doctor blade gap during the cast. It is obvious from the results that the viscosity was lower for the experimental batch. There is not enough data to determine whether this was due to the change in plasticizer or to the higher temperature at the time of the measurement. Certainly part of the viscosity reduction was due to the higher slip temperature. It appears, however, that almost a 1000 cP difference is not completely attributable to the higher temperature.

Table 2 includes the data and observations made on the tapes which resulted from the casting runs.

Table 2 – Green Tape Results

Property:	**Control:**	**Experimental:**
Thickness:		
Thin:	0.0102 -0.0144"	0.0095-0.0100"
Thick:	0.0161-0.0217"	0.0226-0.0242"
Green Bulk Density (GBD)	2.475 g/cc	2.56 g/cc
Green Oxide Only Density (GOOD)	1.975 g/cc	2.04 g/cc
Flexibility	High	Higher
Tackiness	None	Slight
Strength	Excellent	Excellent

The control batch of tape exhibited a typical curling at the edges of the cast which in turn caused some of the thickness variation observed. The thinner control tape exhibited less of this thickness variation. The curling of the experimental tape using the new plasticizer was not as severe and resulted in better thickness uniformity for both the thin and the thick tapes. A possible explanation for the better thickness uniformity with the experimental tape could be due to the slightly higher flexibility. It was also observed for the experimental lot that there was a faint residual film on the carrier and on the bottom side of the tape itself which is an indication that the plasticizer concentration may be slightly high. The tackiness observed is another indication of this. This ties in well with the T_g measurements which indicated that the S-2075 is a better plasticizer than the butyl benzyl phthalate. This leads to the conclusion that less plasticizer is needed to yield the same tape flexibility.

The green bulk density values are averages of several measurements on both the thin and thick tapes. The green oxide only density values are calculated from the GBD measurements and eliminate the organic content. Both the GBD and the GOOD values are significantly higher for the experimental tape. This is an indication that the actual packing density in the experimental tape is better. It is possible that the S-2075 is acting as a secondary dispersant in conjunction with the fish oil. Further experimental tests would have to be conducted to validate this.

The results for the sintering evaluation and comparison are presented in Table 3 as follows:

Table 3 - Sintering Results

Property:	**Control:**	**Experimental:**
Fired Bulk Density	3.618 g/cc	3.622 g/cc
Shrinkage:		
Along Tape	21%	20%
Across Tape	20%	20%
Thickness	10 – 14%	11- 15%

The results for the fired bulk density for the batches made with the standard butyl benzyl phthalate and the triethylene glycol di-2ethylhexanoate plasticizers are well within the experimental error limits of the measurements and can be considered equivalent. Likewise the fired shrinkage in the X, Y, and Z directions are also well within the experimental error limits. In addition all of the samples which were sintered were completely free of any defects.

Summary and Conclusions: Tape casting formulations for a standard 92% alumina ceramic have been evaluated using an environmentally friendly plasticizer. The results were compared with the industry standard plasticizer: butyl benzyl phthalate. The green tape properties including green bulk density, thickness uniformity, flexibility and strength were all found to be equal to or better than the standard. The final sintered density, shrinkage during sintering, and fired part quality also were equal to or better than the samples prepared using the industry standard. Based on these results it has been determined that the triethylene glycol di-2-ethylhexanoate Type 1 plasticizer can be used as a substitute for the butyl benzyl phthalate in tape casting formulations. As a substitute, Solutia S-2075 triethylene glycol di-2-ethylhexanoate is found to have better compatibility and efficiency with polyvinyl butyral as measured by glass transition temperature than butyl benzyl phthalate as well as other phthalate plasticizers.

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1. Aluminum Oxide, A-16SG, Almatis, Leetsdale, PA 15056
2. EPK Kaolin, Zemex Industrial Minerals, Inc., Atlanta, GA 30338
3. Nytal® 400 Talc, R.T. Vanderbilt Co., Inc., Norwalk, CT 06856
4. Blown Menhaden Fish Oil, Grade Z-3, W.G. Smith, Inc., Cleveland, OH 44113
5. Xylenes, Reagent Grade
6. Ethyl Alcohol, 95% Denatured, Reagent Grade
7. Santicizer® 160, Ferro Corporation, Bridgeport, NJ 08014
8. UCON50HB2000, The Dow Chemical Co., Danbury, CT 06817
9. Butvar® B-98, Solutia Inc., St. Louis, MO 63166
10. S-2075, Solutia, Inc., St. Louis, MO 63166
11. G10JRM, Silicone Coated Mylar, Richard E. Mistler, Inc., Yardley, PA 19067.