

DIALLYL PHTHALATE MOLDING COMPOUNDS Processing Guide

Chemistry and Features

Allylic resins are noted for good molding characteristics and the ability to retain electrical and mechanical properties under adverse environmental conditions. In large part, both the processing and final properties are derived from the structures of the polymers on which the molding compounds are based.

The polymers derived from diallyl phthalate consist of polycyclic structures. The polymer of diallyl ortho-phthalate (DAP) exemplifies this structure. All evidence indicates a uniformly cyclized structure with pendant allylic unsaturation spaced at regular intervals along the chain as shown in Figure 1.

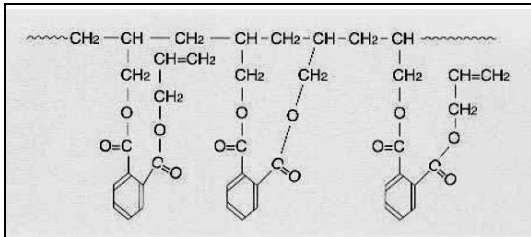


Figure 1: Molecular Structure of DAP Resin

The consequences of this structure are:

1. Solid polymers melting rather sharply at about 70°C.
2. High melt viscosity despite relatively low molecular weight (ca. 10,000) arising from the rigid, densely packed cyclic units.
3. Near equivalency of all crosslinking groups provides simple curing kinetics.
4. A cured structure which is thermally stable and resistant to a variety of chemicals.

The polymer of diallyl meta-phthalate ("iso-DAP") is similar in structure, differing only in that cyclization does not occur quite as regularly as in the ortho-phthalate resin. Crosslink density achievable in cured iso-DAP resin is thus higher with an attendant increase in the ultimate glass transition

temperature (T_g). Fully cured DAP resin exhibits an ultimate T_g of about 165°C, while a T_g approaching 250°C is attainable with iso-DAP resin. Both of these polymers are important commercially.

Flow Rheology

Compounds based on DAP or iso-DAP resins are designed to process well in all types of molding equipment except long fiber DAP/iso-DAP which are not designed for injection molding equipment. Compounds are available in a variety of flow ranges, from very stiff for compression molding to very soft for injection molding. Their plasticities are normally measured by a special transfer molding procedure known as Mesa Spiral Flow. This test provides an indication of the relative ability of the compound to flow and fill molds. Brabender torque rheometer measurements are sometimes utilized to characterize both flow and curing properties.



Figure 2: Mesa Spiral

Storage

DAP compounds exhibit excellent shelf life under normal factory storage conditions, and no special precautions are necessary beyond keeping them in closed containers and avoiding exposure to temperatures over 90°F (32°C). Moldability and molded properties are generally not significantly affected for at least 1 year provided that the material is stored at or below 70°F (21°C).

Compounds based on iso-DAP resin possess greater reactivity, and therefore cold storage of these materials is recommended. Normal storage life is about 6 months when kept at or below 40°F (4°C). The material should be brought to room temperature before containers are opened to prevent the introduction of condensed moisture from the atmosphere.

Preforming or Screw Plasticating

Diallyl phthalate compounds can be charged directly into the mold cavity in granular or flake form. This practice may be desirable in the case of single cavity compression molds for large components, as well as with presses utilizing automatic powder loading. The compound should be accurately weighed or volumetrically metered for each molding cycle.

For the production of small and medium-sized parts with multi-cavity compression molds or transfer molds, preforms are generally preferred. Preforms can be made in many shapes and sizes by compaction of the molding material in a die. Preforms are easier to handle and can be more readily preheated than loosely packed bulk material.

Granular diallyl phthalate compounds are easily preformed by any of the usual types of hydraulic or mechanical preforming presses or screw plasticating machines. Screw plastication combines both preforming and preheating in one process.

Automatic preformers require free-flowing granular compounds in order to maintain weight consistency and rapid cycles. Materials with the lowest bulk densities, such as those containing long glass fibers, cannot usually be preformed automatically in conventional equipment. These often require auxiliary feeding equipment or a manual weighing and pressing operation.

Preheating

The molding compounds should be heated before being loaded into the mold. This reduces the time required to bring the material to a plastic state and allows shorter molding cycles than are possible with cold material. Preheating can increase productivity by 20 to 40% depending on the

geometry of the part and the material being molded. The preheated material also flows more easily and uniformly and generally requires less pressure. Other benefits of preheating include smoother molded surfaces and enhanced physical properties.

Preheating can be accomplished by warming loose powder in an oven. Forced-draft ovens are preferred to avoid hot spots. The most commonly used preheating methods are dielectric (HF) heating of a densely packed perform or frictional heating using a screw plasticator.

Preheat temperature is one of the most critical molding parameters. The temperature should be optimized to provide the easiest flow. This usually means raising the temperature of the compound until obvious precure or short shots occur in molding, and then dropping back 10 to 15°F.

Molding Methods

In general, diallyl phthalate compounds can be processed by all conventional thermoset molding methods, such as compression, transfer or injection molding except for long glass fiber diallyl phthalate which is not designed for injection molding. Most thermoset molding machines are suitable for these materials without the need for special equipment.

Compression molding is the best choice for long-fiber grades, because there are no runners and gates to cause reinforcement breakdown. Compression moldings generally provide the best isotropy.

Transfer or plunger molding is a predominant method used with DAP compounds. This method is particularly useful for parts that contain molded-in inserts. Strength may be somewhat lower



Figure 3: Injection Molding Presses

and shrinkage somewhat higher than that of parts molded by compression. The magnitudes of these differences are dependent on runner and gate design plus the flow pattern in the mold cavity.

Formulations are available to take full advantage of the high productivity of injection molding. They offer excellent barrel and nozzle stability with fast cure in the mold and also possess excellent storage stability.

In injection or transfer molding, a sound molding requires complete cavity filling and adequate packing before gelation. Mold filling time should neither be too short; to avoid trapping air or overheating material through friction, nor too long, to avoid gelation before the cavity is completely packed. If molding conditions do not allow sufficient packing pressure, part strength will be compromised. Other properties including dimensions are affected by cavity packing pressure as well.

The curing time should be long enough for the part to be ejected from the mold without distortion.

Mold cavities should be well polished and plated with hard chrome to ensure easy release. A draft of 1/2 degree on cavity surfaces that are perpendicular to the mold parting line will facilitate easy part demolding. All transfer and injection molds must be properly vented at the parting line, and knock-out pins may need axial flat faces to provide more venting for deep recesses.

Suggested Start-Up Conditions

Molding conditions may vary depending on the shape of the part, mold design, and composition of the material. Suggested start-up conditions and approximate curing times along with an injection molding trouble shooting guide are provided in Figure 6 and Figure 7..

Postcuring and Degassing

Molded parts normally never attain complete cure under commercial conditions. In most cases, conditions are established which produce an acceptable degree of cure and attendant physical properties when the parts

are removed from the mold. It is not necessary to postcure molded parts unless a specific application requires that resistance to high-temperature or chemical exposures be maximized or that the by-products of the curing initiators be driven off.

Figure 4:

T _g Development in 3-1-525F		
Mold Temp. °C	Cure Time S	T _g * °C
165	30	104
	105	124
	180	128
175	30	142
	105	157
	180	161

*Onset of T_g region measured by dynamic mechanical analysis. Injection molded test bars with nominal thickness of 1/2 inch.

The glass transition temperature, T_g, in diallyl phthalates is a function of the degree of interchain crosslinking, which depends primarily on molding and postcuring times and temperatures. Data showing the dependence of T_g on curing conditions are shown in Figure 4 for a typical DAP compound. These data demonstrate the importance of using the highest practical mold temperature.

The retention of physical properties at elevated temperatures is governed by the T_g. For maximum thermal stability and retention of physical properties at high temperatures, molded parts can be postcured. This should be performed in a forced-draft oven having good temperature control and outside venting.

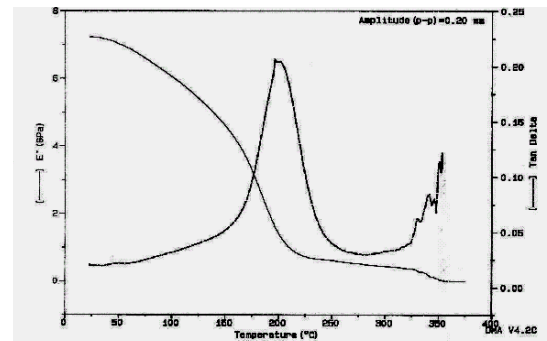


Figure 5: Modulus Behavior of Well Cured 3-1-525F

Optimum postcuring conditions are determined by the specific application requirements. When determining the oven temperature cycle, it is important to note that lower temperatures generally result in less thermal stress and less discoloration of the

part. Most cycles begin at 275°F (135°C) and the temperature is gradually raised to avoid exceeding the T_g . The rate of temperature rise should be as fast as permissible without visual signs of degradation such as blistering or cracking. A final oven temperature of 175°C is usually sufficient to complete the crosslinking reactions without significant discoloration. For applications requiring minimum outgassing, the final oven temperature should be at least equal to the maximum

service temperature and the parts should be baked from 2 to 8 hours at this final temperature or until the rate of weight loss is negligible.

Technical Assistance

Please contact your Sumitomo Bakelite representative if technical assistance is desired.

Figure 6: Suggested Start-Up Conditions

COMPRESSION/TRANSFER	PARAMETER SETTINGS
Preforming Pressure Preheat Temperature Preheating Time (HF) Mold Temperature Molding Pressure – Compression -Transfer Cure Time	8,000-12,000 psi (544-816 bar) 210-240°F (100-115°C) ≤ 45 s 320-350°F (160-180°C) 3,500-6,000 psi (238-408 bar) 2,500-5,000 psi (170-340 bar) 45-70 s (per 3.2 mm thickness)
INJECTION	PARAMETER SETTINGS
Barrel Temperatures R/M/N* Screw Speed Back Pressure Material Temperature Mold Temperature Injection Pressure Hold Pressure (Cavity) Cure Time	140/170/190°F (60/77/88°C) 50 rpm 700-2,200 psi (50-150 bar) 210-240°F (100-115°C) 320-350°F (160-180°C) Adjust to inject material in 5-15 s $\frac{1}{2}$ of injection pressure 40 s (per 3.2 mm thickness)
*Rear Zone/ Middle Zone/ Nozzle	

Figure 7: Injection Molding Trouble Shooting Guide

	Non Fills	Porosity	Staining	Gas Burns	Parts Stick	Blisters	Warpage	Excessive Flash	Excessive Shrinkage	Erratic Injection	Nozzle Cure	Sprue Sticking
Injection Pressure	↑	↑			↓	↑	↑	↓	↑	↑		↓
Back Pressure (Plasticizing)		↓	↓			↑			↑		↓	
Clamp Pressure								↑				
Material Feed Setting	↑	↑				↑		↓				
Nozzel Temperature		↓								↓	↓	↑
Barrel Temperature										↓	↓	
Mold Temperature	↓	↓	↓	↓	↓	↑			↓			↑
Injection Pressure Time							↑					
Injection Hold Pressure Time									↑			
Cure Time			↑		↑	↑	↑		↑			↑
Screw Plastication Delay											↑	
Material Flow	↑						↓	↓		↓	↓	
Poilish Sprue Bushing												↑
Gates Size	↑					↑	↑					
Venting		↑	↑	↑		↑						
Injection Speed		↓		↓								
Polish Mold			↑		↑							