Processing polyester resins for coatings applications

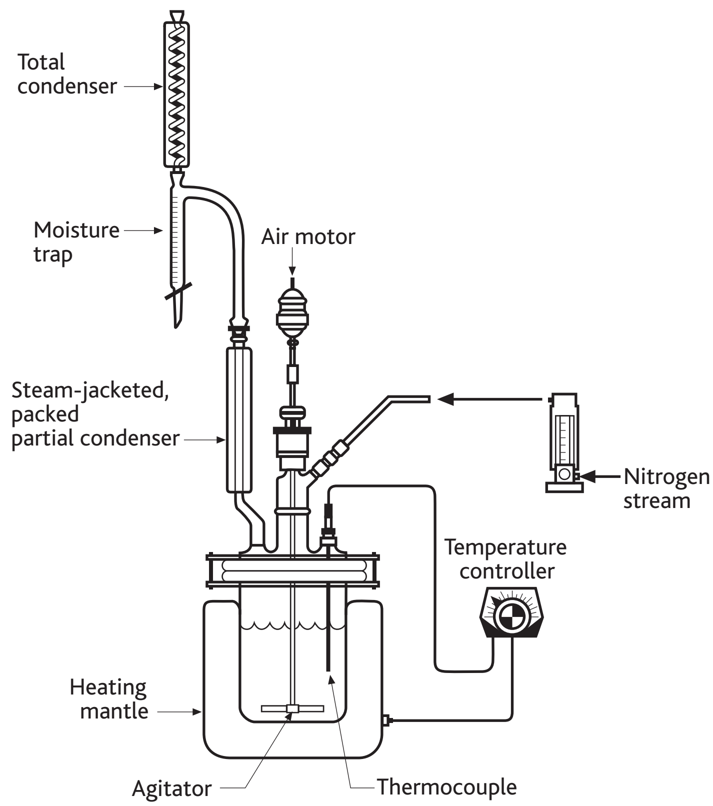
Because of individual preferences and equipment availability, there are many variations in the laboratory equipment and methods used to process saturated and unsaturated polyester resins. The equipment and general procedures for manual, computer-automated, and pilot scale resin processing used by the Eastman Resin Intermediates Technical Service Laboratory are described in this brochure.

- Manually controlled laboratory equipment
- Computer-controlled laboratory equipment
- Pilot plant equipment
- Equipment and suppliers
- General synthesis considerations
- Typical properties of polyester resin intermediates

Manually controlled laboratory equipment

Polyester resins are prepared in 2-L reaction kettles with matching kettle tops (Figure 1). Alternatively, round-bottom, four-neck reaction flasks of 1- to 5-L capacity may be used. Each setup is equipped with an air-driven stirrer, thermocouple, nitrogen-inlet, and a steam-jacketed partial condenser (Liebig™ condenser) charged with a packing material, such as Raschig™ rings.

Figure 1
Manual apparatus for polyester resin synthesis



A Barrett™ moisture trap is installed at the top of the partial condenser and beneath a double-cooling condenser jacketed with chilled water. The flask is heated by means of an electrical-heating mantle, and the temperature is monitored via a type J thermocouple with a Powers™ 535 1/4 DIN process controller. A complete parts list is provided in Table 1.

Table 1 **Equipment and suppliers**[a]

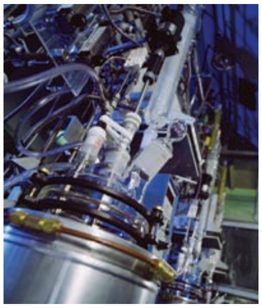
Automated	Manual	Supplier	Description	Product no.
X	X	Lab Glass Vineland, NJ www.lab-glass.com	Adapter, off-set, 24/40 joint	LG-1580-100
X	X		Adapter, thermometer, and inlet tube, PTFE, 24/25 inner member	LG-10447T-106
X			Adapter, thermometer, and inlet tube, PTFE, 10/18 inner member	LG-10447T-100
X			Spherical ground joint, socket only, 12 in. length w/bottom cut at 45° angle (special order drip tube)	LG-1041-116-S
X	X		Reaction vessel lid, 4 neck, O-ring flange, 24/40 side necks, 34/45 center neck, and 34/45 front neck at 75° angle from horizontal	LG-8077-S
X	X		Reaction vessel, cylindrical, O-ring flange, 2,000 mL capacity	LG-8075-100
X	X		Condenser, double cooling, 400-mm jacket, 24/40 joint (request 3/8 in. Swagelok™ inlet and outlet for automated setup)	LG-4811-106
X	X		Condenser, Liebig, 400-mm jacket, 24/40 joint (request 3/8 in. Swagelok™ inlet and outlet for automated setup)	LG-5220-106
X			Adapter for head and column temperature thermocouples (special order)	Z-LG-1983-1030-732919
X			Moisture trap for automated setup (special order)	Z-LG-1740-DWG-21098
	X		Moisture trap, Barrett™, w/2-mm PTFE plug, 20 mL capacity	LG-9076T-102
X	X		Sleeve, PTFE, 24/40 joint	LG-1038T-114
X	X		Sleeve, PTFE, 34/45 joint	LG-1038T-122
X	X		Stopper, full length, penny head, hollow, 34/45 joint	LG-10300-116
X	X		Heating mantle, reaction kettle, 2,000 mL, w/type J thermocouple installed at factory (special order)	LG-8883-106
X	X	Ace Glass Louisville, KY www.aceglass.com	Bearing, Trubore, PTFE, Ace-Thred, 10-mm, 34/45 joint (modified with 10-mm hose connect above 34/45 joint)	8066-50 (8066-737)
X	X		CAPFE™ O-ring	7855-88
X	X		Clamp, reaction flask, 2 piece	6508-11
X			Flexible stirring shaft coupling for 10-mm stirring shaft, ½-in. motor shaft	8125-13
	X	George C. Paris Co., Inc. Knoxville, TN www.georgeparisco.com	Powers 535 1/4 DIN process controller	535-2000-000000

(Continued)

Table 1 (Continued) **Equipment and suppliers[a]**

Automated	Manual	Supplier	Description	Product no.
X	X	Brooks Instrument Division, Emerson Electric Co. Hatfield, PA www.emersonprocess.com/brooks	1350 series Sho-Rate™ low flow indicator, 316 SST, w/valve, no tube	1350EHC5KCG1A
X	X		Model 1350 tube, 0-2 SCFH air at 70°F and 14.7 PSIA	2-65A (code B)
	X	Gast Manufacturing Inc. Benton Harbor, MI www.gastmanufacturing.com	Air motor, 1 HP, ½-in. shaft	4AM-FRV-13C
	X	Omega Engineering, Inc. Stamford, CT www.omega.com	Type J thermocouple, SS sheath, ¼-in. diameter, grounded junction, 12-in. length	JTSS-14(G)-12
X			Quick disconnect RTD probe, 100 ohm, ⅛-in. diameter, 18-in. long	PR-13-2-100-1/8-18-E
X		Thermo Electric Saddle Brook, NJ www.thermo-electric-direct.com	4-in. Type J, 316SS, flexible thermocouple	J116G-316-O-4-3A
X			13-in. Type J, 316SS, flexible thermocouple	J116G-316-O-13-3A
X		Glas-Col Apparatus Co. Terre Haute, IN www.glascol.com	HST10 series geared stir motor, 1/17 HP, 417 max. rpm, 5.4 lb-in. torque, 6:1 ratio	HST10-6M
X			HST10 series controller with isolation transformer with isolated rpm and torque output and 4-20 mA input	HST10-6
X			Plug and extension cable for x-y output of HST10	099D A052060
X		Thermo NESLAB Portsmouth, NH www.neslab.com	EX-110 heating bath/circulator, 5-L (1.3-gal) bath volume, w/digital controller for RS-232 interface	EX-110
X			RTE-210 refrigerated bath/circulator w/ digital controller for RS-232 interface	RTE-210
X		Mykrolis Corporation Bedford, MA www.mykrolis.com	Tylan™ FC-260V mass flow controller, 4S, 800 sccm N_2 ¼-in. Swagelok™	Tylan™ FC260V
X		Parker Hannifin Corporation Skinner Valve Div. Cleveland, OH www.skinnervalve.com	7321 Pilot operated brass solenoid valve—normally closed, NBR seals, ¼-in. orifice, 5-300 psi, 10 watts, 120/60 (110/50) volts (Hz)	73212BN2MNOONO C111P3
X		Mettler Toledo Columbus, OH www.mt.com	PM 4800 DeltaRange™ balance with RS-232 interface	PM 4800 DeltaRange™ balance
X		Argonaut Technologies Systems, Inc. Indianapolis, IN www.camile.com	Camile™ PC-based data acquisition and control hardware and software	Camile™ 2500 hardware; Camile™ TG v. 3.7 software

[a]*List of equipment used by the Eastman Resin Intermediates Technical Service Laboratory to assemble manual and automated resin processing apparatuses. Although they may continue to be used in the Eastman laboratory, some of the equipment has been discontinued. Contact the respective supplier for a suitable replacement.*



Computer-controlled laboratory equipment

Components

The automated resin-processing apparatus (Figures 2 and 3) consists of three components: resin-processing equipment, computer, and interface device.

Figure 2
Diagram of automated apparatus for polyester resin synthesis

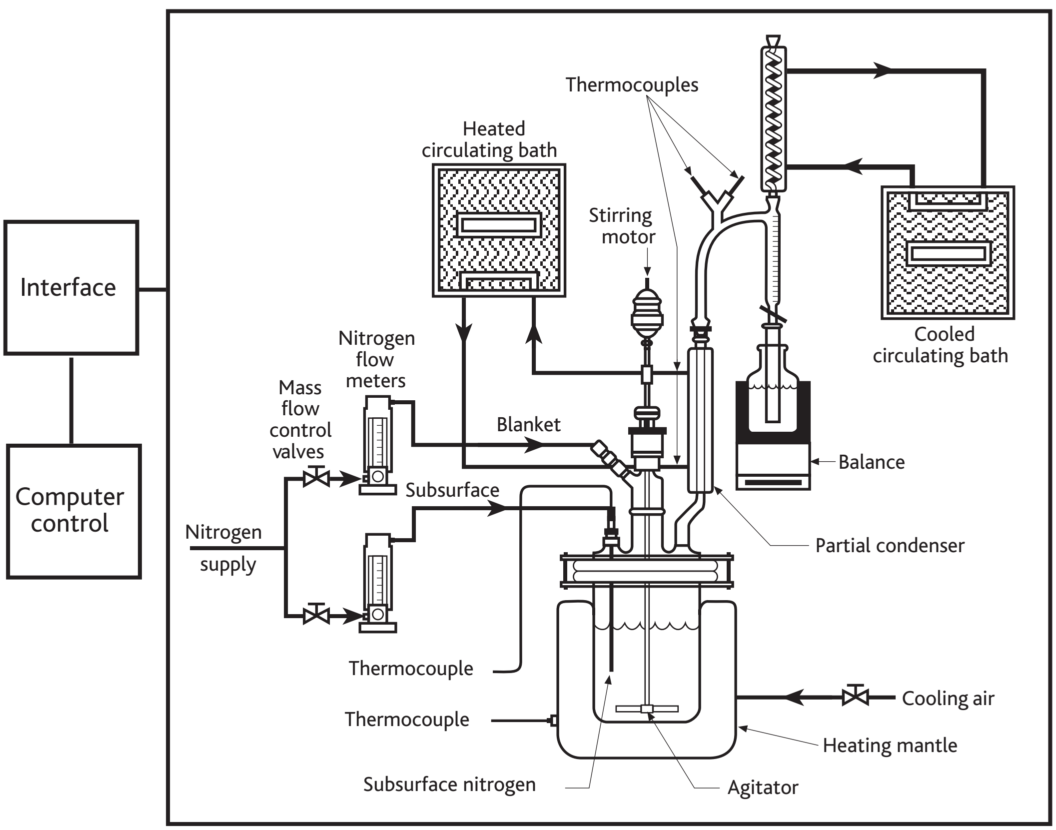
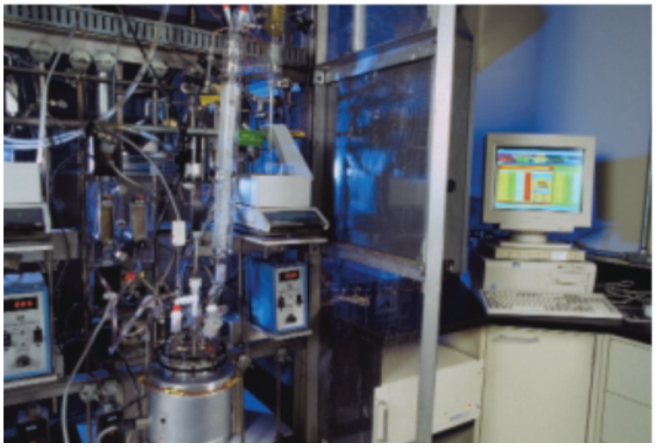


Figure 3
Automated apparatus for polyester resin synthesis



The resin-processing equipment is essentially the same as with a manual setup but with some notable enhancements (see Table 1). Circulating hot oil baths replace steam heating for the partial condensers, providing more precise temperature control. The total condenser incorporates a circulating bath with a coolant mixture of propylene glycol and water to obtain lower-than-ambient temperatures, if necessary. Balances measure the amount of distillate collected. Mass flow control valves deliver nitrogen more precisely. The heating mantles, retrofitted with compressed air lines, aid in temperature control and cooldowns, enhancing safety. The stirring motors are equipped with monitors that measure torque as well as speed, and resistance temperature detector (RTD) thermocouples measure resin temperature.

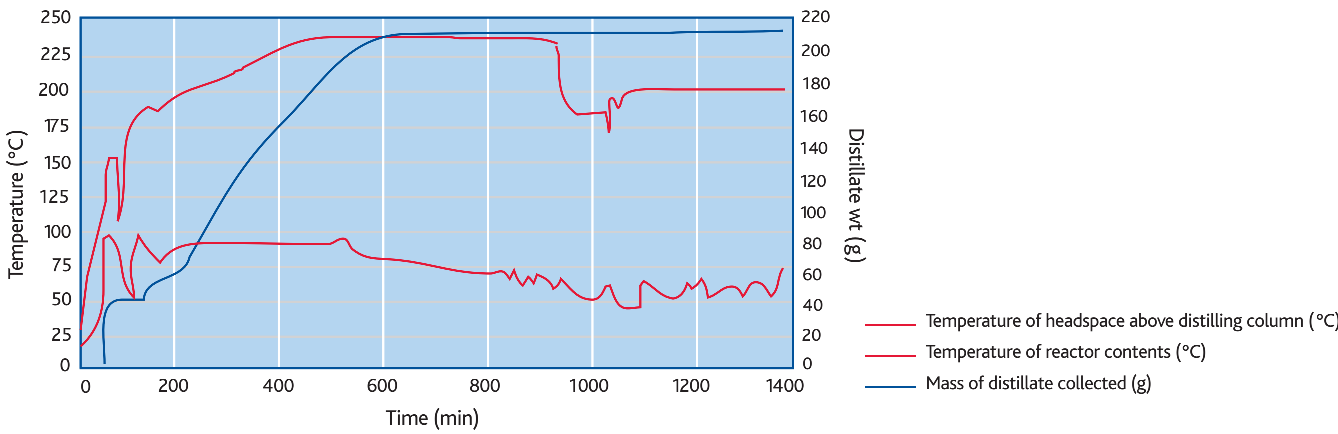
The computer and interface, working together, have the ability to control and monitor peripherals used in resin synthesis. The automated setups use an Intel Pentium™ processor-based computer running Microsoft Windows 7™ operating system with Camile™ TG v.5.2 data acquisition and control software for running user-defined programs. The Camile 2500 hardware interface handles the task of delivering signals back and forth from the sensors and control devices to the computer. A balance interface is also required to process data to and from the computer for multiple balances.

Capabilities

Automated resin processing provides many new capabilities to laboratory resin production. The system can keep log files that record resin-processing data. While a resin cook is running, real-time data can be accessed and displayed as graphs. Such data displays and logs are useful in the laboratory and in historical analysis.

Further data manipulation within a spreadsheet is possible to generate graphs and data tables. Figure 4 is an example of data graphed from a polyester resin cook. Graphs are useful for determining cook times and cause-effect relationships among process variables.

Figure 4
Eastman™ powder coating resin formulation PC-17-4N reaction profile



Advantages

The capabilities of automated resin processing provide many advantages. Because of safety and control sequences, it is possible to cook resins with less user supervision. Another advantage of computer-controlled resin synthesis is reproducibility. Once a resin cook has been well characterized, the system can be programmed to re-create the conditions (cook time, heat, stirring) to duplicate a resin precisely. An example of resins duplicated on the automated resin processing system is shown in Table 2.

Table 2 **Reproducibility of Eastman resin formulation PC-17-4N[a]**

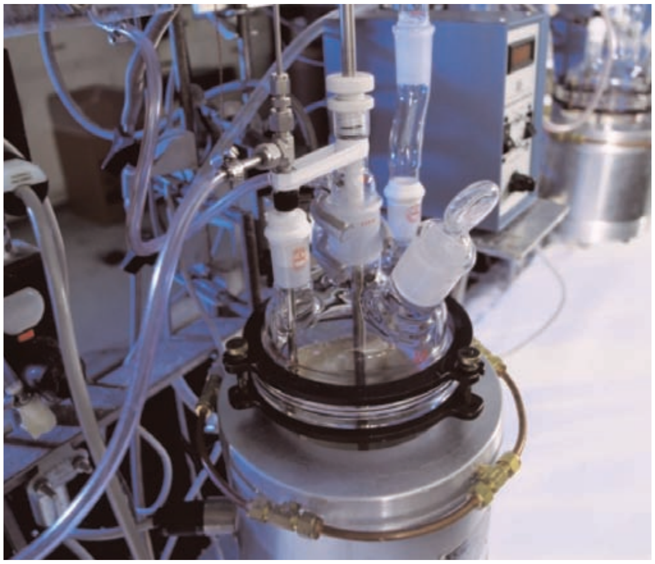
Repeat number	Acid number (mg KOH/g resin)	Hydroxyl number (mg KOH/g resin	Molecular weight[b] (g/mol)			ICI viscosity[d] (poise)
			Mn	Mw	T_g[c] (°C)	
1	75.9	0	2,808	8,513	69	27.2
2	76.8	1	2,719	8,387	70	27.6
3	73.7	0	2,986	9,123	70	29.2
4	74.3	0	2,710	8,757	70	28.4
5	73.5	0	2,804	8,710	70	28.4
6	75.1	2	2,856	8,630	68	29.2
Mean	74.9	0.5	2,814	8,687	69.5	28.3
Std. Dev.	1.3	0.8	101	253	0.8	0.8

[a] *Reference Eastman publication N-281.*

[b] *Determined using Gel Permeation Chromatography with a refractive index detector.*

[c] *Determined by Differential Scanning Calorimeter. Midpoint of second heat reported. Scan rate of 20°C/min. from 0°–100°C with nitrogen purge.*

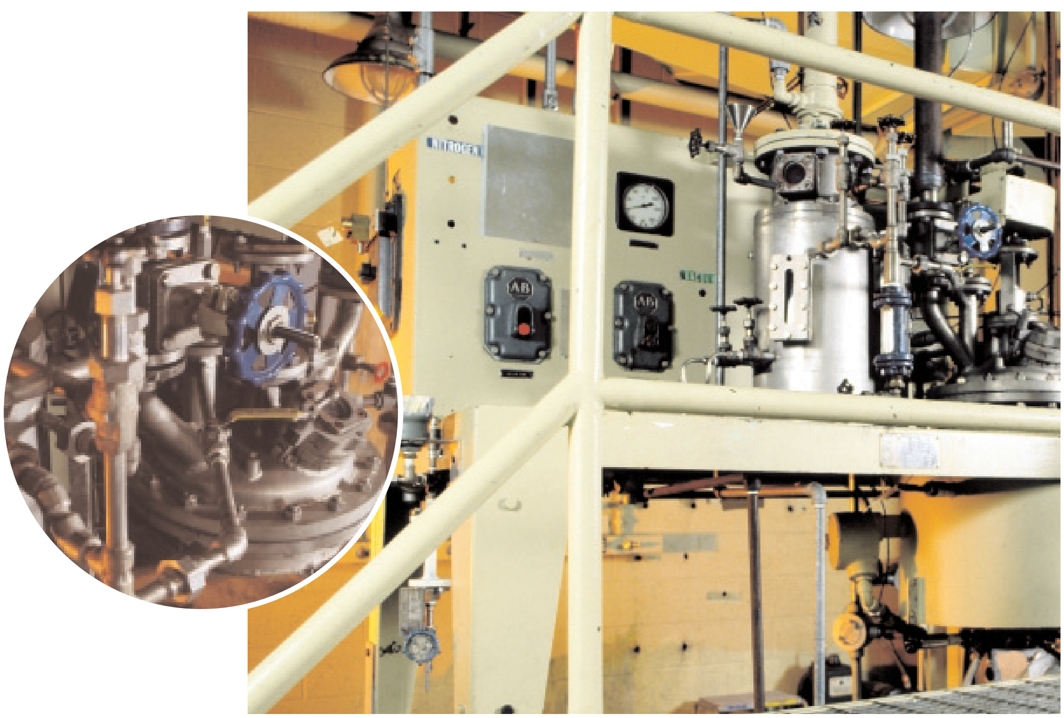
[d] *Determined at 200°C with 0–40 spindle.*



Pilot plant equipment

Pilot scale quantities of polyester resin are made in a modified, 10-gallon Brighton™ reactor model E-110A (manufactured by Trinity Industries, Inc., Brighton Custom Fabricating Div., Cincinnati, Ohio). It is equipped with a specially designed overhead condenser assembly constructed at Eastman. A picture of the Brighton™ reactor is shown in Figure 5. Some of the features of this reactor are described on page 8.

Figure 5
Brighton reactor



Vessel

The vessel is constructed of 316 stainless steel. Heat is applied by radiant electric heaters that are attached to the outside walls of the vessel and enclosed in a shell. Initial melting of the reactants is accomplished with steam through a coiled tube located within the vessel. Cooling of the reactor contents can be accomplished by water circulation through the coil as well. Baffles are attached to the vessel walls to help with agitation and minimize foaming of the reaction mixture.

Agitator

The turbine-type agitator is driven by a ½-hp, 220/440-volt explosion proof motor equipped with a variable-speed drive unit. An ammeter, installed in the electrical circuit of the motor, measures the electrical current flow (amps). This measurement can be used as an indication of viscosity buildup in the latter stages of the cook.

Distillation columns

The unit is equipped with two adjacent, distillation columns of the double-pipe, vertical type. The primary column is filled with packing material. The secondary column, used only toward the end of the cook, is not packed. Both distillation columns are steam-heated.

An inverted U-tube installed above the distillation columns opens downward into the total condenser, an American Standard™ No. 302 SSCF heat exchanger (ITT Standard, Buffalo, N.Y.). The total condenser discharges the condensate into a Brighton™ decanter-receiver.

Thinning tank

The reactor is equipped for direct discharge of molten material or letdown of the reaction mixture into a 20-gallon type 304 stainless steel dilution tank. The tank is jacketed for steam heating, and the contents can be blanketed with nitrogen. A ⅓-hp explosion proof gear motor powers the turbine-type agitator. Baffles are attached to the vessel walls to help with agitation and minimize foaming. A reflux condenser is available to return solvent to the solution, and a thermocouple provides the temperature of the contents. A pressure filtration system is available for filtering resin solutions as they are pumped from the dilution tank. Or the pump can be put on a closed loop to return material to the tank for added mixing.

General synthesis considerations

The following techniques have been found generally applicable in polyester synthesis with various glycol and acid intermediates. Some useful properties of polyester resin intermediates are listed in Table 3.

Inert gas

The use of an inert gas is essential in the synthesis of high-quality polyester resins; high-purity nitrogen is preferred. The flow rate is carefully adjusted with a laboratory flow meter or mass flow valve. With the inlet tube positioned above the reactants in the vessel, the nitrogen flow is started prior to the first application of heat.

The preferred flow rate of nitrogen depends on the size of the reaction vessel and the polyester resin being prepared. Generally, the flow rate is within the range of 0.1 to 0.4 L/min per liter of vessel capacity (0.2–0.8 ft^3/h/L). Slower flow rates are used at the beginning of the cook to avoid excessive entrainment of monomeric reactants. Faster flow rates and subsurface delivery of nitrogen are sometimes used toward the end of the cook to facilitate removal of water and other volatile impurities as the resin molecular weight builds.

Azeotropic solvent

The use of xylene as an azeotropic solvent accelerates the removal of water. Also, the xylene condensate serves to clean the interior overhead parts of the reactor by washing down any solid reactants that otherwise might accumulate. Xylene should be used judiciously with Eastman NPG™ glycol because it forms a trinary azeotrope with NPG and water. The trinary azeotrope can remove unreacted glycol from the reactor. An amount of xylene not more than 1–2 wt% of the total charge can be added during the initial phase of the reaction. As the reaction progresses and the evolution of water slows, more xylene may be added, provided it is removed by nitrogen sparging toward the end of the cook cycle.

Distillation column

The use of a heated distillation column (or partial condenser) is strongly advised. It helps prevent the loss of more volatile reactants while allowing the efficient removal of water. Control is important because loss of reactants can alter the molecular weight and thus the performance properties of the polyester. For maximum efficiency, the distillation column should contain a packing material, such as Raschig™ rings. This increases the condensation area of the column and physically opposes the flow of vapors entrained in the inert gas stream. Maintaining an internal column temperature of 103°–105°C is desirable. Toward the end of the reaction, the packed column may be replaced by an open distillation column to facilitate the removal of water, azeotropic solvent, and other volatile impurities.

Summary

Each method of polyester resin processing has its unique advantages. Manually controlled laboratory equipment allows the most flexibility and is best suited for new, uncharacterized formulations. Computer-controlled laboratory equipment is ideal for producing duplicates of well-characterized resins and for resins that process over long periods, such as unsaturated polyesters and powder coating resins. Pilot plant equipment allows large quantities of a resin to be produced in the shortest amount of time. These three means of resin processing, coupled with the general synthesis tips, allow efficient and timely production of resins for laboratory experimentation.

Table 3 **Typical properties of polyester resin intermediates**

Compound	Molecular weight	Solidification or melting point, °C	Boiling point, 760 mm, °C	Wt/Vol, 20°C		Specific gravity 20°/20°C
				Lb/U.S. gal	Kg/L	
Glycols						
2-Butyl-2-ethyl-1,3-propanediol (BEPD)	160.26	39–40	262	—	—	—
Eastman™ 1,4-CHDM[a] (cyclohexanedimethanol)	144.21	41–61	293	9.59	1.15	1.50[b]
Ethylene glycol (EG)	62.07	–13	199	9.28	1.11	1.12
Propylene glycol (PG, 1,2-propanediol)	76.10	–60	187	8.64	1.04	1.04
1,3-Butylene glycol	90.12	25	207	8.39	1.00	1.00
Diethylene glycol (DEG)	106.12	–8	246	9.31	1.12	1.12
Eastman™ HPHP glycol	204.27	46–50	293	—	—	—
Eastman NPG™ glycol[c]	104.15	124–130	210	8.19	0.98	0.98
Eastman TMPD™ glycol	146.22	46–55	215	7.73	0.93	0.93[d]
Pentaerythritol[e]	136.15	269	Sublimes	—	—	—
Trimethylolethane[e]	120.15	135	204	—	—	—
Trimethylolpropane[e]	134.18	58	160	—	—	—
Acids and anhydrides						
Adipic acid	146.14	152	265 (100 mm)	11.4	1.37	1.37
Eastman™ 1,4-CHDA (cyclohexanedicarboxylic acid)	172.21	164–167	—	—	—	1.38
Fumaric acid	116.07	200 (sublimes)	287 (sealed tube)	13.6	1.63	1.63
Eastman™ PIA (purified isophthalic acid)	166.13	346	Sublimes	12.8	1.53	1.54
Maleic anhydride	98.06	54	200	12.3	1.47	1.47
Phthalic anhydride	148.12	131	284	12.7	1.52	1.52
5-SSIPA (sodiosulfoisophthalic acid)	268.19	>300	—	—	—	—
Eastman™ PTA (terephthalic acid)	166.13	Sublimes	>300 (sublimes)	—	—	—
Trimellitic anhydridee	192.14	165	390	12.8	1.54	1.54

[a] *For ease of handling, Eastman™ CHDM-D90 glycol, a mixture of 90 parts Eastman™ CHDM glycol and 10 parts water is available.*

[b] *20°/4°C*

[c] *For ease of handling, Eastman NPG™ 90 glycol, a mixture of 90 parts Eastman NPG™ glycol and 10 parts water, is available.*

[d] *55°/15°C*

[e] *A multifunctional (f>=3) polyester monomer (brancher)*

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