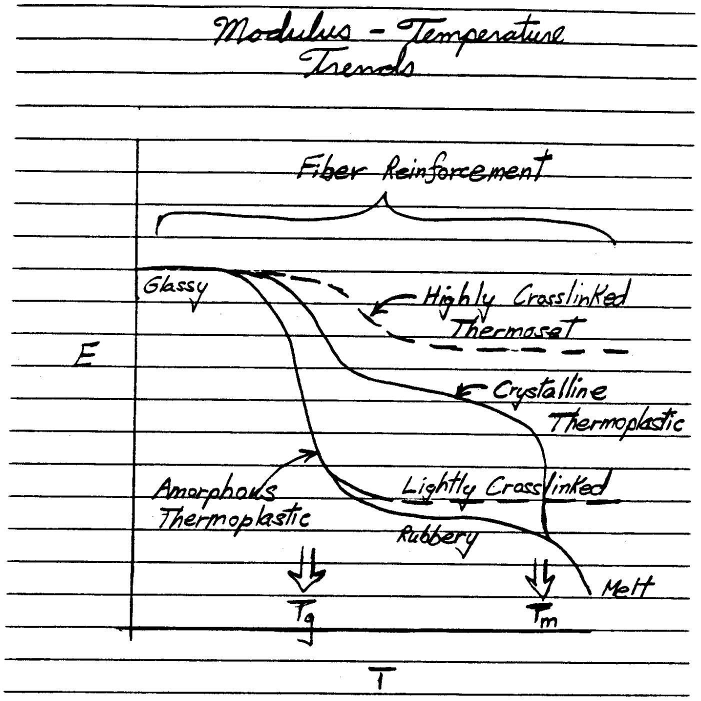
2.2 Matrix



Transverse Property Estimates
(unidirectional composites)

- **Try Parallel Rule of Mixtures Model:**

  $1/\sigma = v_m/\sigma_m + v_f/\sigma_f$ $1/E = v_m/E_m + v_f/E_f$

  Sample Calculation

  - **Carbon Fiber (Hercules AS 4)**

    E_f = 32 msi , σ_{fu} = 450 ksi , ε_{fu} = 0.012

    $E_{f,90^\circ}$ = 2 msi (perhaps) and $\sigma_{fu\cdot 90^\circ}$ = 12 ksi ?? (interface controls)

  - **Epoxy Matrix**

    E_m = 350 ksi , σ_{mu} = 12 ksi , ε_{mu} = 0.034

  - **Composite (v_f = 0.60, unidirectional)**

    $1/\sigma = 0.4/12 + 0.6/12$ or $\sigma_{c,90^\circ}$ = 12 ksi (interface contols)

    $1/E = 0.4/0.35 + 0.6/2 = 0.7$ msi

> Matrix or Interface Dominated

Target Neat Resin Properties for Structural Composites

(obtained from NASA Langley)

Mechanical (Room Temperature)

- $E_m \geq$ 500 ksi (3.5 GPa)
- $\sigma_{my} \geq$ 10 ksi (69 MPa)
- $G_{Ic} \geq$ 5 in lb / in^2 (0.9 kJ / m^2) (mode one fracture energy)
- $\tau_i = \sigma_{my} / 2$

Environmental

- High Service Temperature (e.g. > 177 °C)
- Low Moisture Gain (e.g. < 1 %)
- Solvent Resistance (e.g. chlorinated solvents)
- Light Stable

Processing

- Low t, T, P (time, temperature, pressure)
- Low shrinkage (e.g. < 3 %)
- No Byproducts / Volatiles
- No Toxicity
- Good Shelf Life (e.g. months)
- Good Tack and Drape

General

- Low Density (e.g. < 1.5 g / cm^3)
- Low Cost (e.g. < $ 2 / lb)

2.3.1 Epoxies

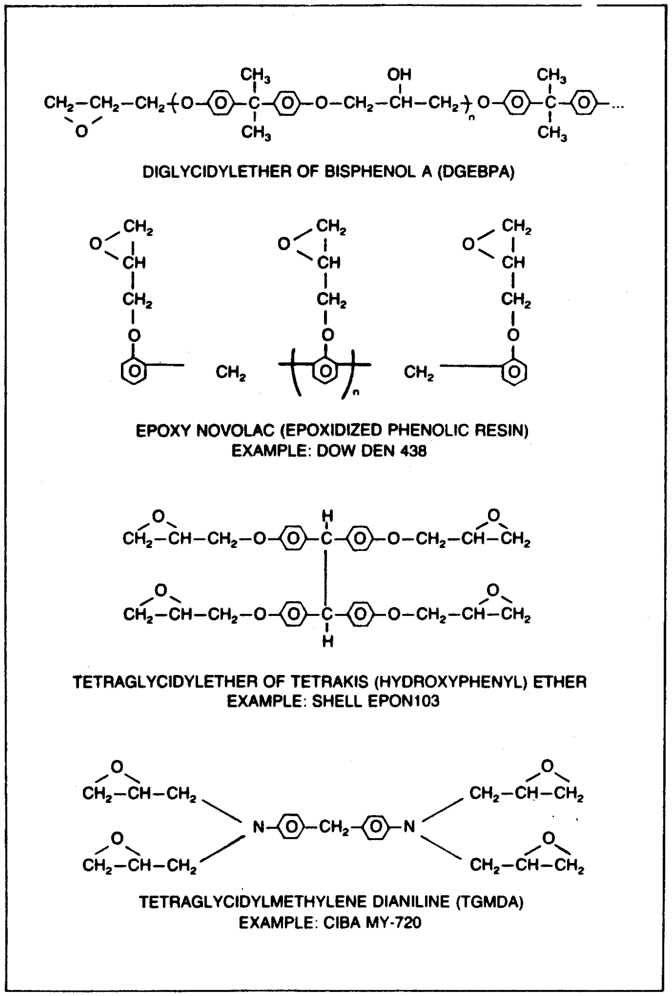
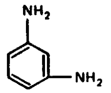
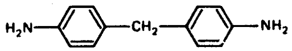


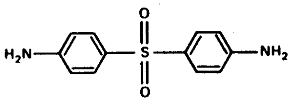
Figure 2-4. Major epoxy resin systems.



Metaphenylenediamine (MPDA)



Methylenedianiline (MDA)



4, 4'-diaminodiphenylsulfone (DDS)

Table 2-2
Comparison of Properties for Epoxies Versus Polyesters

ADVANTAGES OF EPOXIES	
Adhesion	-Outstanding
Strength	-Excellent
Corrosion Protection	-Outstanding
Chemical Resistance	-Excellent
Shrinkage on Cure	-Very Low
Electrical Properties	-Excellent
Versatility	-Excellent
Toughness	-Good
Toxicity (cured)	-None known
Taste (cured)	-None
Heat Resistance	-Good
Weather Resistance	-Excellent for Protection
Color/Odor	-Good
Fatigue Strength	-Excellent
DISADVANTAGES OF EPOXIES	
Cost	-Medium to High
Ease of Handling	-Medium to Difficult
Toxicity (uncured)	-Problems
Weather Resistance	-Poor for Appearance

Table 3 Typical epoxy resin curing agents for composite fabrication

	General curing conditions, 25 °C (80 °F)										
		Typical cure				Post cure(b)				Heat distortion temperature(c)	
				Temperature			Temperature				
Curing agent type and typical products	Concentration, phr(a)	Time, h	days	°C	°F	Time, h	°C	°F	Pot life at 25 °C, h	°C	°F
Aliphatic amines and derivatives, room-temperature cure:											
Diethylenetriamine (DTA)	12	...	7	25	80	1	200	390	¼-½	124	255
Triethylenetetramine (TETA)	14	...	7	25	80	1	200	390	¼-½	123	255
Polyamides (Versamides)(d)	30-50	...	7	25	80	None	...	...	2-3	55	130
Amine adducts(e)	26	...	4	25	80	1	150	300	¼-½	120	250
Aliphatic/cycloaliphatic amines, moderate-temperature cure:											
Diethylaminopropylamine (DEAPA)	8	0.5	...	115	240	None	...	...	3-4	100	212
Bis (*p*-aminocyclohexyl) methane (PACM-20)	29	1.0	...	150	300	3	150	300	1.5	149	300
Isophorone diamine (IPD)	23	1.0	...	100	212	3	150	300	1.0	146	295
n-aminoethylpiperazine (AEP)	20	1.0	...	150	300	3	150	300	¼-½	110	230
2-ethyl-4-methyl imidazole (EMI-24)	10	8.0	...	60	140	None	...	...	4-6	110	230
Same	4	4.0	...	60	140	2	150	300	20 +	160	320
Aromatic amines, elevated-temperature cure:											
m-phenylenediamine (MPDA)	14	2.0 + 2.0	...	80(175)/150	300	2	150	300	5-6	150	300
4,4′-methylenedianiline (MDA)	28	2.0 + 2.0	...	80(175)/150	300	2	150	300	5-6	160	320
4,4′-diaminodiphenylsulfone (DDS) + 1phr BF_3 − MEA	30(f)	2.0 + 2.0	...	125(257)/200	390	2	200	390	(g)	175	350
Aromatic amine eutectics(h)	20	2.0 + 2.0	...	80(175)/150	300	2	150	300	6-8	145	290
Carboxylic acid anhydrides, elevated-temperature cure:											
Hexahydrophthalic anhydride (HHPA) + 1phr BDMA(i)	78	3.0 + 1.0	...	90(195)/150	300	3	200	390	24	132	270
Nadic methyl anhydride (NMA) − 1phr BDMA	90	3.0 + 1.0	...	120(250)/150	300	3	200	390	60-80	144	290
Chlorendic anhydride (CA)(j)	117	Gel + 4.0	...	25(80)/150	300	3	200	390	(j)	197	385
Dodecenylsuccinic anhydride (DDSA) + 1phr BDMA	134	4.0 + 1.0	...	90(195)/150	300	3	200	390	120	74	165
Methyltetrahydrophthalic anhydride (MTHPA) + 1phr BDMA	80	1.0 + 1.0	...	100(212)/150	300	4	150	300	24	130	265
Catalytic Lewis acids, elevated-temperature cure:											
Boron trifluoride monoethylamine (BF_3-MEA)	3	3.0 + 4.0	...	120(250)/200	390	4	200	390	>250	174	345
Latent curing agents, elevated-temperature cure:											
Dicyanamide (DICY)	6	1.0	...	175	350	1.0	175	350	∞	135	275(k)

(a) Parts per 100 parts resin by weight for the DGEBPA-WPE = 189. (b) Used to obtain heat distortion temperature. Post cure should be made at or above HDT. (c) By ASTM D 648 (Ref 18) (d) Based on polyamide (Versamide) resin; other grades are available. (e) Based on curing agent U, Shell Chemical Co. Numerous proprietary types are available. (f) Less than stoichiometric (33 phr) because BF_3-MEA also assists curing. (g) Mixture is too viscous for this measurement. Prepreg useful life is 10 to 20 days. (h) Data on curing agent Z, Shell Chemical Co. Many others available. (i) BDMA = benzyldimethylamine. (j)Chlorendic anhydride seldom used alone or at stoichiometry (203 phr) due to fast gel time (k) T_g as measured by thermal mechanical analysis on a laminate. Source: Ref 19, 20

Table 8 Wet and dry properties of carbon fiber laminates(a)

				0° flexural properties			
	Test temperatur,			Ultimate		Modulus	
Resin system	°C	°F	Test condition	MPa	ksi	GPa	10^6 psi
TGETPM(b)/DGEBPA, 3:1/DDS	25	80	Dry	1850	267	149	21.6
	93	200	Dry	1460	211	140	20.3
	93	200	Wet	1360	197	170	24.5
	149	300	Dry	1320	191	138	19.9
	149	300	Wet	990	143	163	23.6
	205	400	Dry	1120	162	137	19.8
	205	400	Wet	650	93.5	162	23.4
TGMDA/DGEBPA, 3:1/DDS	25	80	Dry	1640	237	128	18.5
	93	200	Dry	1440	208	127	18.4
	93	200	Wet	1160	168	132	19.1
	149	300	Dry	1260	182	125	18.0
	149	300	Wet	720	104	129	18.6
	205	400	Dry	800	115	112	16.2
	205	400	Wet	370	54	113	16.4

(a) Unidirectional carbon fiber laminates, (AS4-6K) normalized to 62 vol % fiber. Source: Ref 11. (b) See Fig. 2 for chemical structure.

Table 6 Properties of wet lay-up heat-cured laminates prepared using various curing agents(a)

				Normalized flexural properties(d)			
		Test temperature		Ultimate		Modulus	
Epoxy resin	Curing agent(b) and concentration(c)	°C	°F	MPa	ksi	GPa	10^6 psi
DGEBPA	MPDA(14)	25	80	627	90.5	24.8	3.6
		150	300	434	63	21.3	3.1
DGEBPA	MDA(28)	25	80	526	76	19.4	2.8
		150	300	304	44	15.9	2.3
DGEBPA	Aromatic amine eutectic(e)	25	80	556	82	21.8	3.2
DGEBPA	DDS(20) BF_3-MEA(1)	25	80	471	68	20.8	3.0
		127	260	394	57	18.0	2.6
DGEBPA	NMA(90) BDMA(1)	25	80	476	69	20.5	3.0
		150	300	241	35	16.3	2.3
		260	500	78	11.3	7.2	1.0
DGEBPA	HHPA(78) BDMA(1)	25	80	491	71	20.1	2.9
DGEBPA	Chlorendic anhydride(117)	25	80	391	57	23.5	3.4
TGMDA	HHPA(110)	25	80	510	74	...	...
		170	340	225	32.5	...	...

(a) Data on 181-style, E-glass cloth, Volan A finish. (b) Structural formulas appear in Fig. 1-8, chemical names in Table 3. (c) Parts per 100 parts resin by weight. (d) Normalized to 67 wt% glass. (e) Many products of this type are commercially available. Data presented based on Curing Agent Z, Shell Chemical Company. (f) Data on N,N′-tetraglycidylmethylenedianiline, glass fabric type not specified (Ref 27). Source: Ref 18

Polyesters

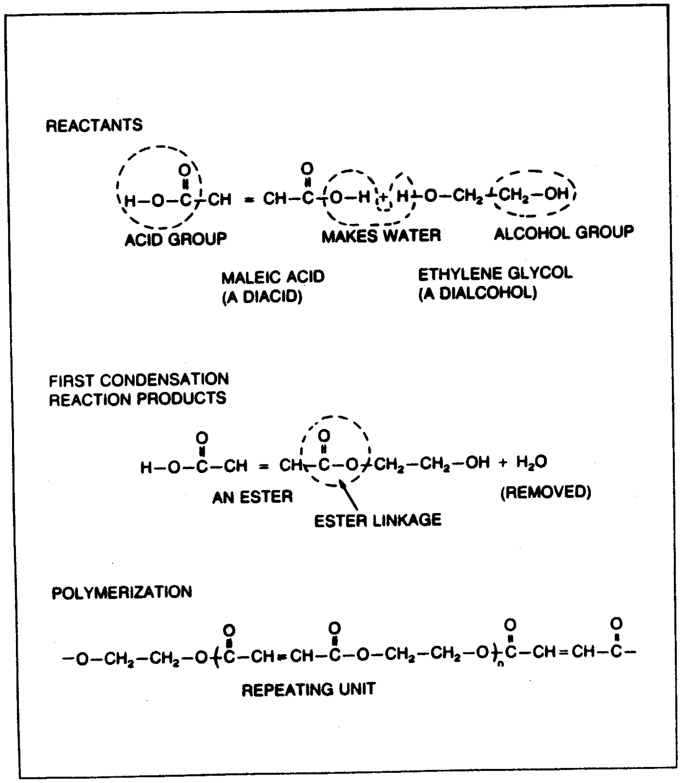


Figure 2-1. Condensation polymerization of a polyester.

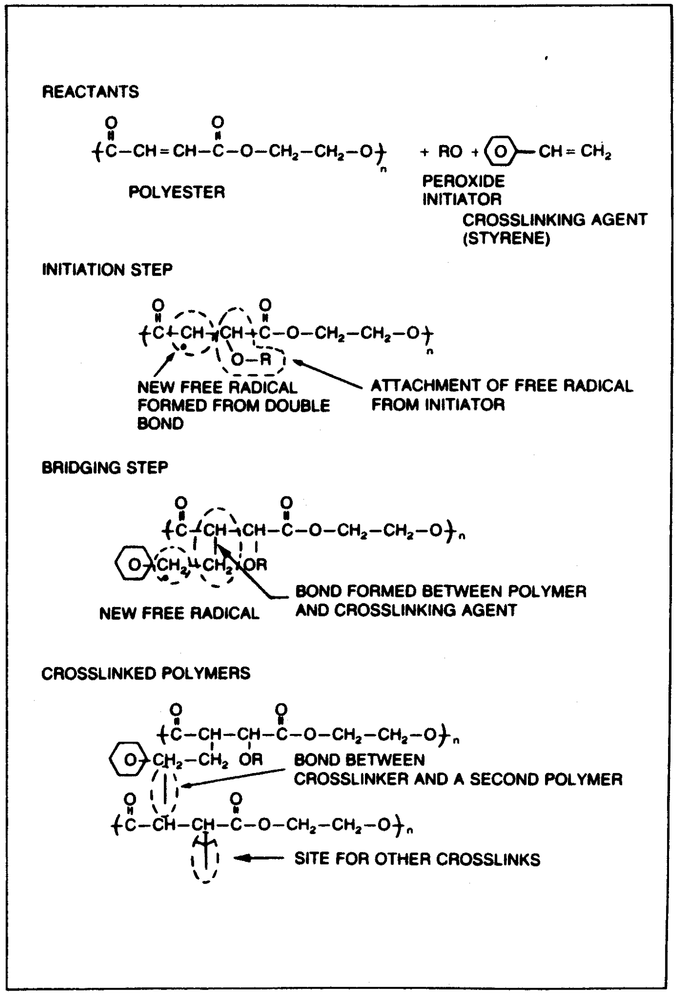
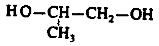
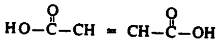
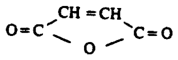
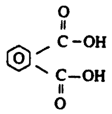
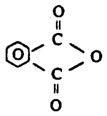
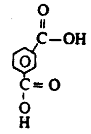
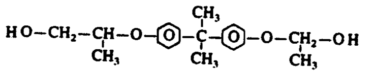


***Figure 2-2.** Addition (or free-radical) crosslinking of polyester.*

Table 2-1
Choices of Reactants for Polyester Resins

Reactant	CHEMICAL STRUCTURE	Advantages
Ethylene Glycol	$HO-CH_2-CH_2-OH$	*Basic reactant
Propylene Glycol	 $HO-\underset{CH_3}{CH}-CH_2-OH$	*More compatible with styrene than ethylene glycol
Maleic Acid (also Fumaric Acid)	 $HO-\overset{O}{C}-CH = CH-\overset{O}{C}-OH$	*Flexible *Low cost
Maleic Anhydride		*~~No~~ Less water byproduct
Orthophthalic Acid (Ortho)		*Rigid *Relatively low cost
Orthophthalic Anhydride		*Rigid *~~No~~ Less water byproduct
Isophthalic Acid (ISO)		*Resilient (tough) *Thermal stability
Bisphenol A-based		

HERE ARE THE FOUR BASIC BUILDING BLOCKS IN POLYESTER RESINS AND HOW THEY CAN BE MANIPULATED TO OBTAIN SPECIALTY FORMULATIONS

Building Blocks	Ingredients	Characteristics
Unsaturated anhydrides and dibasicacids	a - maleic anhyd~~y~~ride	a - lowest cost, moderately high heat deflection temperature (HDT) --- (*)
	b - fumaric acid	b - highest reactivity (crosslinking), higher HDT*, more rigidity.
Saturated anhydrides and dibasic acids	a - phthalic (ortho-phthalic) anhydride	a - lowest cost, moderately high HDT*, provides stiffness, high flex, and tensile strength.
	b - isophthalic acid	b - higher tensile and flex strength, better chemical and water resistance.
	c - adipic acid, azelaic acid, and sebacic acid	c - flexibility (toughness, resilience, impact strength) adipic acid is lowest in cost of flexibilizing acids.
	d - chlorendic anhydride	d - flame retardance.
	e - nadic methyl anhydride	e - very high HDT*.
	f - tetrachlorophthalic anhydride	f - flame retardance.
Glycols	a - propylene glycol	a - lowest cost, good water resistance and flexibility, compatibility with styrene.
	b - dipropylene glycol	b - flexibility and toughness.
	c - ethylene glycol	c - high heat resistance, tensile strength, low cost.
	d - diethylene glycol	d - greater toughness, impact strength and flexibility.
	e - bisphenol A adduct	e - corrosion resistance, high HDT*, high flex and tensile strength.
	f - hydrogenated bisphenol A adduct	f - corrosion resistance, high HDT*, high flex and tensile strength.
Monomers	a - styrene	a - lowest cost, high reactivity, fairly good HDT*, high flex strength.
	b - diallyl phthalate	b - high heat resistance, long shelf life, low volatility.
	c - methyl methacrylate	c - light stability, good weatherability, fairly high HDT*.
	d - vinyl toluen~~c~~e	d - low volatility, more flexibility, high reactivity.
	e - triallyl cyanurate	e - very high HDT*, high reactivity, high flex and tensile strength.

*HDT — Heat Distortion Temperature

Polyimides

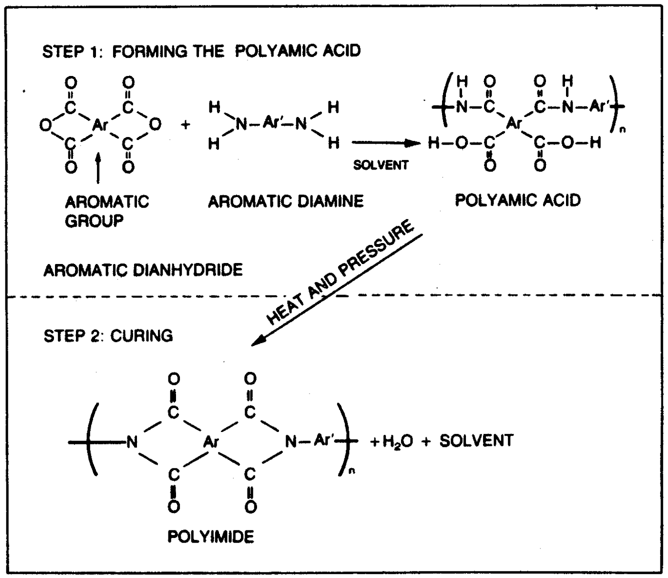


Figure 2-5. General reactions for polyimide formation.

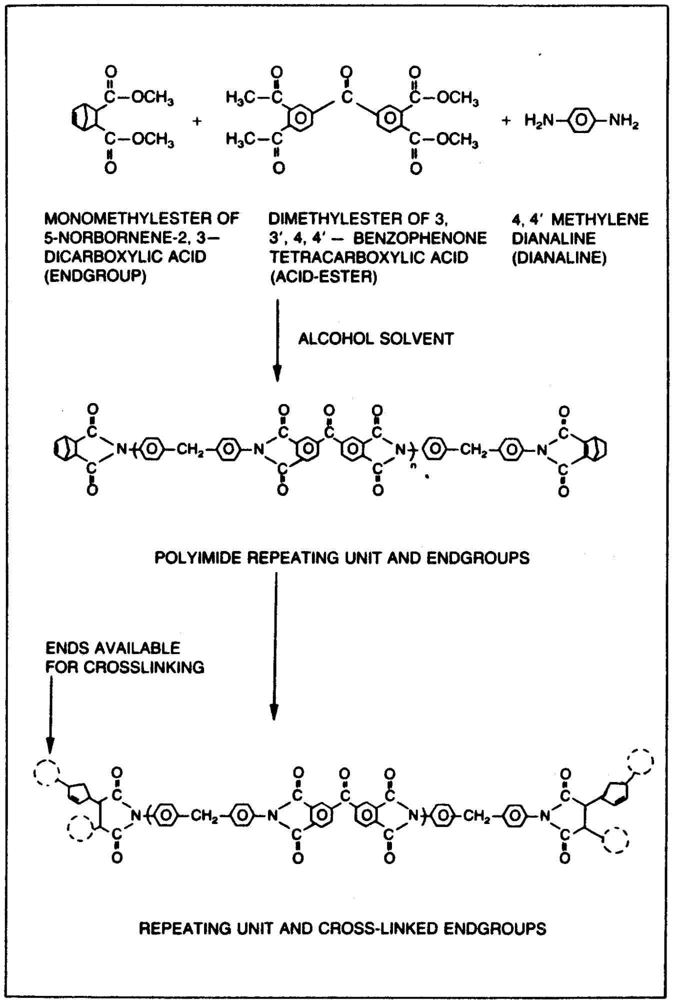


Figure 2-6. End-group crosslinking for PMR-15.

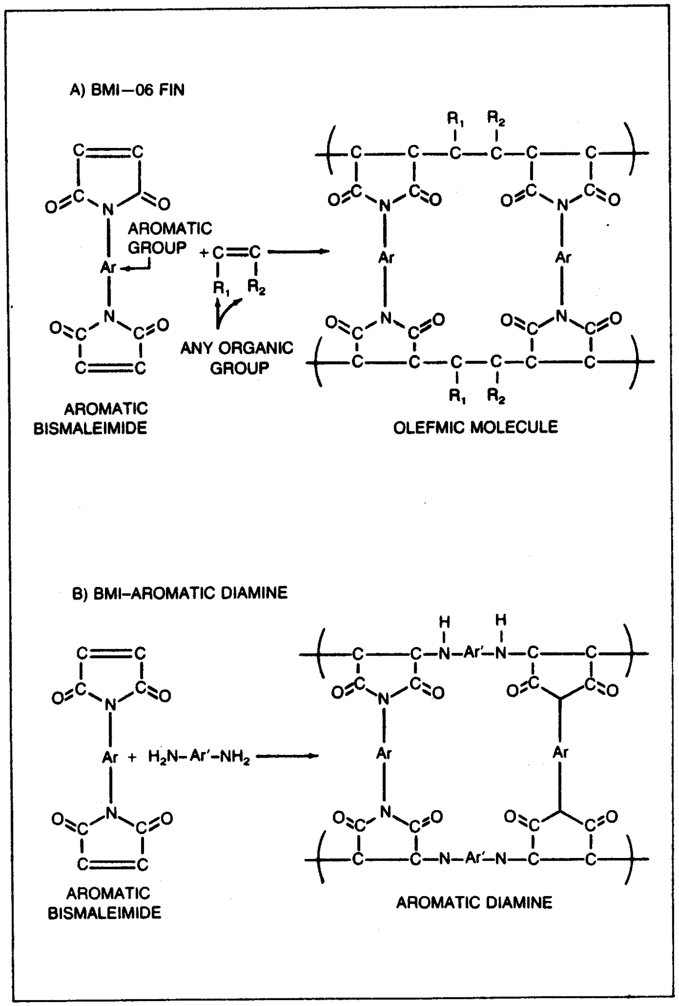


Figure 2-8. Addition crosslinking using bismaleimide (BMI).

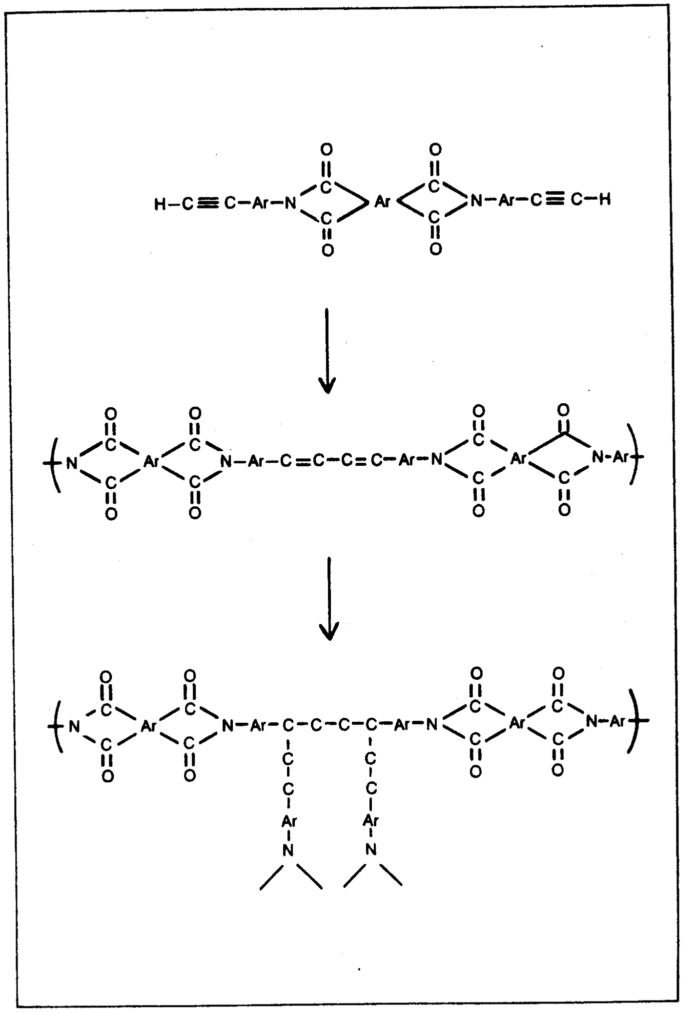


Figure 2-7. Acetylene end-capped polyimide (Thermid 600).

2.5 Phenolics and Carbon Matrices

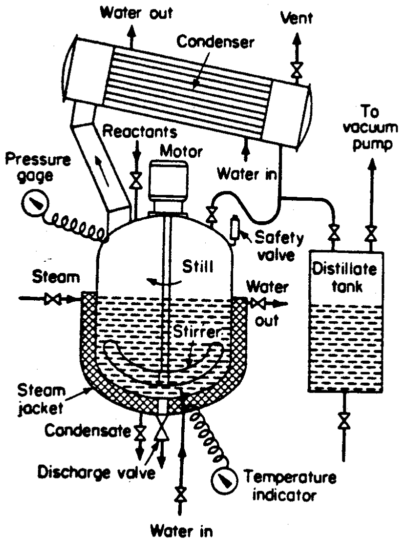
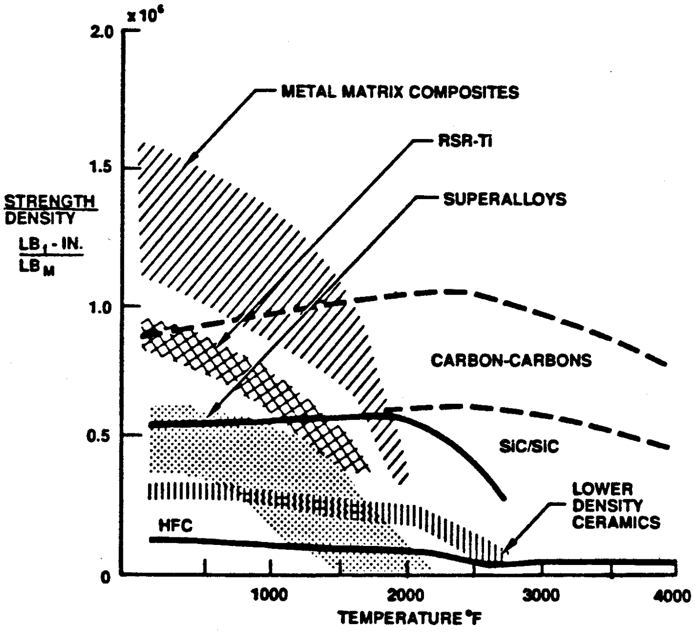
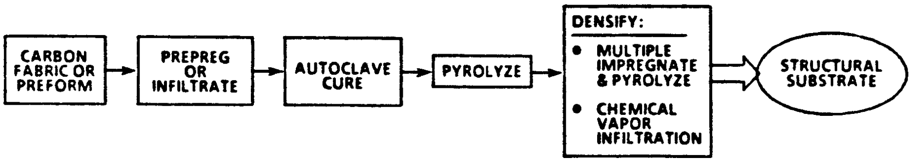


FIGURE 14-9
Reaction vessel for manufacture of phenol-formaldehyde resins [16].

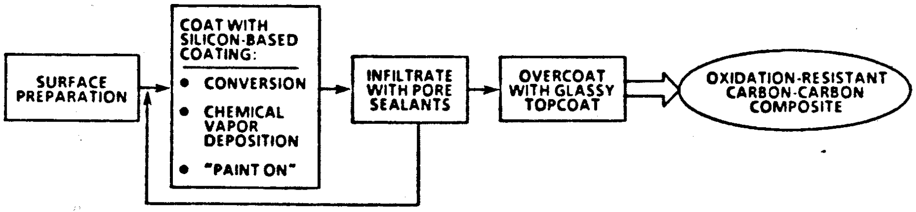


C/C Exhibits the Highest Specific Strength at Elevated Temperature

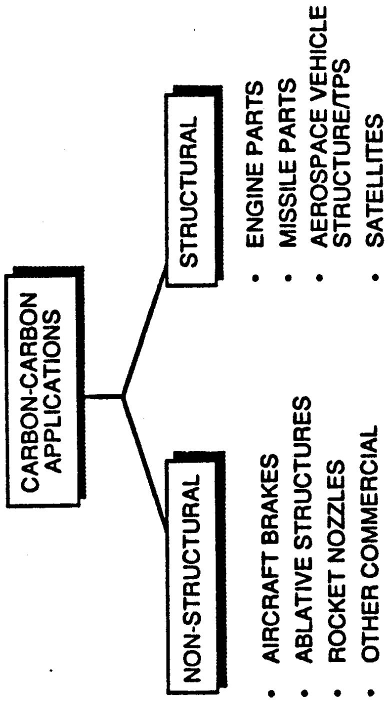
SUBSTRATE FABRICATION:



OXIDATION PROTECTION PROCESSING:



C/C Processing Involves Many Discrete Steps



Types of C/C Applications

Comparative Cost of Selected Engineering Materials

Material	Cost, $/LB
Aluminum Alloys[a]	2-3
Titanium Alloys[a]	20-60
Superalloys[a]	15-70
Refractory Metals[a]	25-250
Organic Matrix Composites[b]	40-750
Carbon/Carbon Composites[b]:	
- Brakes	80-120
- Nozzles, Exit Cones, Nose Cones	600-1500
- Shuttle RCC	6000
- Advanced, Oxidatively Protected (in non-production environment)	2000-15,000

---

a Approximate ranges for simple product forms

b Approximate ranges for a mix of product shapes