Composites and carbon fibers

Topic 2

Reading assignment

- Askeland and Phule, "The Science and Engineering of Materials", 4th Edition, Ch. 16.
- Shakelford, "Introduction to Materials Science for Engineers", 6th Edition, Ch. 14.
- Chung, "Composite Materials", Ch. 2.
- Chung, "Carbon Fiber Composites", Ch. 1, 2 and 3.





























Single fiber tensile strength

- Carbon fiber 3.5 GPa
- Kevlar fiber 3.6 GPa
- E-glass fiber 3.4 GPa
- Steel 1.3 GPa

Specific strength

- Carbon fiber 2.00 GPa Kevlar fiber 2.50 GPa
- E-glass fiber Steel
- 1.31 GPa 0.17 GPa

Single fiber tensile modulus

- Carbon fiber 230 GPa
- Kevlar fiber 60 GPa
- E-glass fiber 22 GPa
- Steel 210 GPa

Sample name	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)	
Thornel P-100	2.2	690	0.3	
P-120	2.4	830	0.3	
Carbonic HM50	2.8	490	0.6	
HM60	3.0	590	0.5	
HM80	3.5	790	0.4	
Torayca M46	2.4	450	0.5	









Material	Applications
Borsic aluminum	Fan blades in engines, other aircraft and aerospace applications
Kevlar™-epony and Kevlar™-polyester	Aircraft, aerospace applications (including space shuttle), boat hulls, sporting groots (including termis rackets, golf club shafts, fishing roots), flak jackets
Graphite-polymer	Aerospace and automotive applications, sporting goods
Glass-çolymer	Lightweight automotive applications, water and marine applications, comosion resistant applications, sporting goods equipment, aircraft and aerospace components





























$$P_{c} = P_{m} + P_{f}$$

$$\boldsymbol{s}_{c}A_{c} = \boldsymbol{s}_{m}A_{m} + \boldsymbol{s}_{f}A_{f}$$

For isostrain condition $(\boldsymbol{e}_{c} = \boldsymbol{e}_{m} = \boldsymbol{e}_{f})$

$$E_{c}\boldsymbol{e}_{c}A_{c} = E_{m}\boldsymbol{e}_{m}A_{m} + E_{f}\boldsymbol{e}_{f}A_{f}$$

$$E_{c} = E_{m}\frac{A_{m}}{A_{c}} + E_{f}\frac{A_{f}}{A_{c}}$$

$$E_{c} = \boldsymbol{n}_{m}E_{m} + \boldsymbol{n}_{f}E_{f}$$





$$X_c = \mathbf{n}_m X_m + \mathbf{n}_f X_f$$

Rule of Mixtures (ROM)

Fraction of load carried by fibers

$$\frac{P_f}{P_c} = \frac{\boldsymbol{s}_f A_f}{\boldsymbol{s}_c A_c} = \frac{E_f \boldsymbol{e}_f A_f}{E_c \boldsymbol{e}_c A_c} = \frac{E_f}{E_c} \boldsymbol{n}_f$$

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Isostress condition

$$S_{c} = S_{m} = S_{f}$$

$$\Delta L_{c} = \Delta L_{m} + \Delta L_{f}$$

$$\frac{\Delta L_{c}}{L_{c}} = \frac{\Delta L_{m}}{L_{c}} + \frac{\Delta L_{f}}{L_{c}}$$

$$L_m = A_m L_c$$
$$L_f = A_f L_c$$

$$\frac{\Delta L_c}{L_c} = \frac{A_m \Delta L_m}{L_m} + \frac{A_f \Delta L_f}{L_f}$$

 $\mathbf{e}_c = \mathbf{n}_m \mathbf{e}_m + \mathbf{n}_f \mathbf{e}_f$
For isostress condition ($\mathbf{s} = E_c \mathbf{e}_c = E_m \mathbf{e}_m = E_f \mathbf{e}_f$),
 $\frac{s}{E_c} = \mathbf{n}_m \frac{\mathbf{s}}{E_m} + \mathbf{n}_f \frac{\mathbf{s}}{E_f}$
 $\frac{1}{E_c} = \frac{\mathbf{n}_m}{E_m} + \frac{\mathbf{n}_f}{E_f}$
 $E_c = \frac{E_m E_f}{\mathbf{n}_m E_f + \mathbf{n}_f E_m}$

$$X_{c} = \frac{X_{m}X_{f}}{\boldsymbol{n}_{m}X_{f} + \boldsymbol{n}_{f}X_{m}}$$

$$E_c^n = \mathbf{n}_t E_l^n + \mathbf{n}_h E_h^n$$

n = 1 lsostrain
n = -1 lsostress
Rule of Mixtures (ROM)

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Fiber-matrix debonding

- Silver-copper alloy matrix
- Carbon fiber reinforcement
- Fracture surface observation (fractography)



Fiber-matrix debonding

- Polymer matrix
- Glass fiber reinforcement



Failure mechanisms

- Failure in fibers (ductile -matrix composites, e.g., polymer-matrix and metalmatrix composites), so a high interfacial strength is desired.
- Failure in matrix (brittle -matrix composites, e.g., ceramic-matrix and carbonmatrix composites), so a low interfacial strength is desired (to allow cracks to deflect along fiber-matrix interface, thereby allowing fibers to pull out for the purpose of increasing the toughness)









Reasons for fiber-matrix interface engineering

- To control fiber-matrix bond strength (shear bond strength)
- To improve wetting of matrix precursor on fiber
- To improve fiber dispersion

Methods for fiber-matrix interface engineering

- Fiber surface treatment
- Dispersant as an additive to the matrix

Methods of fiber surface treatment

- Chemical treatment fiber
- Coating of fiber

	Fiber properties		Composite properties	
Fiber treatment	Wt. loss (%)	Tensile strength loss (%)	Flexural strength loss (%)	ILSS gain (%)
400°C in air (30 min)	0	0	0	18
500°C in air (30 min)	0.4	6	12	50
600°C in air (30 min)	4.5	50	Too weak to test	-
60% HNO ₃ (15 min)	0.2	0	8	11
5.25% NaOCl (30 min)	0.4	1.5	5	30
10-15% NaOCl (15 min)	0.2	0	8	6
15% HClO ₄ (15 min)	0.2	0	12	0
5% KMnO ₄ /10% NaOH (15 min)	0.4	0	15	19
5% KMnO ₄ /10% H ₂ SO ₄ (15 min)	6.0(+)	17	13	95
10% H,O,/20% H,SO4 (15 min)	0.1	5	14	0
42% HNO 3/30% H,SO4 (15 min)	0.1	0	4(+)	0
10% NaClO ₃ /15% NaOH (15 min)	0.2	0	12	12
10% NaClO ₄ /25% H, SO ₄ (15 min)	0.2	2	5(+)	91
15% NaClO/40% H, SO4 (15 min)	0.7	4	15	108
10% Na2Cr2O7/25% H2SO4 (15 min)	0.3	8	15(+)	18
15% Na .Cr.O./40% H.SO. (15 min)	17	27	31	18

Types of polymer-matrix composites

- Thermoplastic-matrix composites
- Thermoset-matrix composites

Lower manufacturing cost of thermoplastic-matrix composites

- no cure
- unlimited shelf-life
- reprocessing possible (for repair and recycling)
- less health risks due to chemicals during processing
- low moisture content
- thermal shaping possible
- weldability (fusion bonding possible)

Better performance of thermoplastic-matrix composites

- high toughness (damage tolerance)
- good hot/wet properties
- high environmental tolerance

Disadvantages of thermoplastic-matrix composites

- limitations in processing methods
- high processing temperatures
- high viscosities
- prepreg (collection of continuous fibers aligned to form a sheet which has been impregnated with the polymer or polymer precursor) being stiff and dry when solvent is not used (i.e., not drapeable or tacky)
- fiber surface treatments less developed

Attractive properties of carbon fiber polymer-matrix composites

- low density (40% lower than aluminum)
- high strength (as strong as high-strength steels)
- high stiffness (stiffer than titanium, yet much lower in density)
- good fatigue resistance (a virtually unlimited life under fatigue loading)
- good creep resistance

Attractive properties of carbon fiber polymer-matrix composites

- low friction coefficient and good wear resistance (a 40 wt.% short carbon fiber nylon-matrix composite has a friction coefficient nearly as low as Teflon and unlubricated wear properties approaching those of lubricated steel)
- toughness and damage tolerance (can be designed by using laminate orientation to be tougher and much more damage tolerant than metals)
- chemical resistance (chemical resistance controlled by the polymer matrix)
- corrosion resistance (impervious to corrosion)

Attractive properties of carbon fiber polymer-matrix composites

- dimensional stability (can be designed for zero coefficient of thermal expansion)
- vibration damping ability (excellent structural damping when compared with metals)
- low electrical resistivity
- high electromagnetic interference (EMI) shielding effectiveness
- high thermal conductivity

Limitation of polymermatrix composites

Inability to resist high temperatures

Carbon-matrix composites

Ability to resist high temperatures

Carbon-carbon (C/C) composites

- Carbon fiber
- Carbon matrix
- Carbon matrix made from pitch or polymer

Carbon matrix precursors

- Pitch
- Resins
- Carbonaceous gases

Conversion of carbon matrix precursor to carbon

- Pyrolysis (also called carbonization)
- Heating at around 1000°C in the absence of oxygen to cause decomposition, like charring















Conversion of carbon to graphite

- Graphitization (i.e., crystallization)
- Heating at 2000°C or above in the absence of oxygen to cause the turbostratic carbon to be converted to graphite (crystalline)















































Methods of making carboncarbon composites

- Carbonization, followed by impregnation of pitch or resin, and repeating the carbonizationimpregnation process again and again until sufficient density has been attained.
- Chemical vapor infiltration (CVI) using a carbonaceous gas, i.e., CVD under a temperature/pressure gradient so as to prevent crust formation, thereby allowing complete infiltration; CVI can be an extra step that follows carbonization-impregnation for the purpose of filling the pores.

Table 2.3 Pitch properties.				
	Carbon yield (%)			
Molecular	0.1 MPa	10 MPa		
weight				
726	45.2	85.9		
782	54.4	86.4		
931	84.5	89.8		
	ble 2.3 Pit Molecular weight 726 782 931	ble 2.3 Pitch property for the property of the		

Grades of pitch

- Isotropic pitch
- Mesophase pitch (liquid crystal form called the mesophase)

Main problem with carbon-carbon composites

Oxidation at high temperatures in the presence of oxygen

Methods for oxidation protection of carbon-carbon composites up to 1700°C

- 1. SiC conversion coating
- 2. Oxidation inhibitors
- 3. Glassy sealant
- 4. Dense SiC or Si₃N₄ overlayer on glassy sealant or SiC conversion coating

SiC conversion coating method

SiC coating (known as SiC conversion coating, due to graded composition from pure SiC at the surface to pure carbon inside)

Methods of applying SiC conversion coating

- Pack cementation,
- Reaction sintering,
- Silicone resin impregnation/pyrolysis, or
- Chemical vapor deposition (CVD) to the outer surface of the composite.

Pack cementation

Packing the composite in a mixture of SiC and Si powders and heat up to 1600°C

Chemical conversion of the outermost surface of the composite to SiC

SiC coating thickness typically 0.3-0.7 mm.

Pack cementation

 $\begin{array}{c} \mathrm{Si}(l) + \mathrm{C} \rightarrow \mathrm{SiC}\\ \mathrm{Si}(\mathrm{g}) + \mathrm{C} \rightarrow \mathrm{SiC}\\ \mathrm{SiO}(\mathrm{g}) + 2\mathrm{C} \rightarrow \mathrm{SiC} + \mathrm{CO}(\mathrm{g}) \end{array}$

Problem with entrapped silicon vaporising.

Reaction sintering

Dipping C/C composite into a suspension of Si powder (10 μ m) in an alcohol solution and then sintering at 1600°C for 4 hours in argon.

Silicone resin impregnation/pyrolysis

Vacuum impregnation and cold isostatic pressing (30,000 psi or 200 MPa) a silicone resin into the matrix of a C/C composite and subsequent pyrolysis at 1600°C for 2 hours in argon.

Note: Silicone is a polymer with silicon atoms as a part of the backbone.

Prior deposition of carbon film (10 μm) by CVD

- Prior to pack cementation, reaction sintering or resin impregnation
- To improve homogeneity of C/C surface
- To ease the reaction with Si

Dense SiC or Si_3N_4 overlayers

- SiC overlayer is more dense than the SiC conversion coating.
- As oxygen barrier
- To control venting of reaction products to the outside
- Made by chemical vapor deposition (CVD)



SiSiC overlayer

- CVD overlayer contains a small percentage of unreacted silicon dispersed in the SiC,
- The excess Si upon oxidation becomes SiO₂, which has a very low oxygen diffusion coefficient.

Advantages of SiC or Si₃N₄

- Thermal expansion compatibility with C/C
- Low oxidation rate
- Thin amorphous SiO₂ scale that grows has low oxygen diffusion coefficient.

SiC or ineffective above 1800°C

- Reactions at the interface between SiO_2 and SiC or Si_3N_4
- Reduction of SiO₂ by carbon to form CO gas.

Oxygen inhibitors

- Oxygen getters
- Glass formers

To provide additional oxidation protection from within by migrating to the outer surface and sealing cracks and voids during oxidation.

Examples of inhibitors

- Elemental Si, Ti and B
- SiC, Ti_5Si_3 and TiB_2
- Alloys such as Si₂TiB₁₄
- Organoborosilazane
 polymer solution

Oxidation of the elemental Si, Ti or B within the carbon matrix forms a viscous glass, which serves as a sealant that flows into the microcracks of the SiC coating.

Boron as an oxidation inhibitor

- Boron is oxidized to form B₂O₃.
- B₂O₃ blocks active sites, such as the edge carbon atoms.
- B₂O₃ forms a mobile diffusion barrier for oxygen.

Oxidation rate

Rate of weight loss

Inhibition factor

Ratio of oxidation rate of untreated carbon to that of the treated carbon Method of introducing oxidation inhibitors to the carbon matrix

Incorporating particulate fillers in the resin or pitch (i) prior to prepregging.

during lay-up and

(ii) during densification cycles.

Glassy sealants

- Glazes comprising mainly silicates (SiO_x) and borates (B₂O₃).
- · Glaze can be filled with SiC particles
- Particularly important if the SiC conversion coating is porous
- Glaze fills microcracks in the dense overlayer

Application of a glassy sealant on top of the SiC conversion coating mainly by slurry brush-on, so that the sealants melt, fill voids and stop oxygen diffusion, and, in some cases, act as oxygen getters.

Effectiveness of borate sealants

- Borates wet C and SiC quite well
- Borates cannot be used above 1200°C due to volatilization
- Borates have poor moisture resistance due to hydrolysis, which results in swelling and crumbling
- Borate has a tendency to galvanically corrode SiC coatings at high temperatures

Modified borate sealants

- The problems of borate can be alleviated by using multicomponent systems such as 10TiO₂.20SiO₂.70B₂O_{3.}
- TiO₂ has a high solubility in B₂O₃ and is used to prevent the volatilization of B₂O₃ and increase the viscosity.
- SiO₂ acts to increase the moisture resistance, reduce B₂O₃ volatility, increase viscosity and prevent corrosion of SiC by B₂O₃.

Dense SiC or Si₃N₄ overlayer

- Applied by CVD.
- On top of glassy sealant or on top of SiC conversion coating
- To control and inhibit transfer of oxygen to the substrate
- To control the venting of reaction products to the outside

Method of oxidation protection of C/C above 1700°C

Four-layer coating scheme:

(1) **Refractory oxide** (e.g., ZrO_2 , HfO_2 , Y_2O_3 , ThO_2) as the outer layer for erosion protection.

(2) ${\rm SiO}_2$ glass inner layer as and oxygen barrier and sealant.

(3) Another refractory oxide layer for isolation of the SiO_2 from the carbide layer underneath.

(4) **Refractory carbide layer** (e.g., TaC, TiC, HfC, ZrC) to interface with the C/C substrate and to provide a carbon diffusion barrier

$$HfC + \frac{3}{2}O_2 \rightarrow HfO_2 + CO$$

Fundamental approaches for oxidation protection of carbons

- Prevention of catalysis
- Retardation of gas access to the carbon
- Inhibition of carbon-gas reactions
- Improvement in the carbon crystalline structure

Carbon matrix precursors

- **Pitch** (preferred for oxidation protection)
- Chemical vapor infiltration (CVI) carbon (preferred for oxidation protection)
- **Resins** (not preferred for oxidation protection)

Effects of carbon fiber on oxidation protection

- Alignment of the matrix molecules near the fibers
- Microstructure of fiber affecting that of matrix
- Microstructure of matrix affecting amount of accessible porosity in the matrix

Disadvantage of coatings on C/C

Degrade room temperature mechanical properties of C/C

Metal-matrix composites

- Better temperature resistance than polymer-matrix composites
- Lower temperature resistance than ceramic-matrix composites
- High fabrication cost compared to polymer-matrix composites
- Low fabrication cost compared to ceramic-matrix composites

TABLE 16-1 Examples and applications of selected dispersionstrengthened composites

System	Applications	
Ag-CdO	Electrical contact materials	
AI-AI2O3	Possible use in nuclear reactors	
Be-BeO	Aerospace and nuclear reactors	
Co-ThO2, Y2O3	Possible creep-resistant magnetic materials	
Ni-20% Cr-ThO2	Turbine engine components	
Pb-Pb0	Battery grids	
Pt-ThO ₂	Filaments, electrical components	
W-ThO2, ZrO2	Filaments, heaters	

Methods of fabricating metal-matrix composites

- Liquid metal infiltration
- Hot pressing above the solidus of the matrix metal
- Powder metallurgy (diffusion bonding)
- Plasma spraying
- Slurry casting







Reaction between metal and reinforcement

- Helps wetting
- Degrades reinforcement
- Reaction product (e.g., a carbide) lining the metalreinforcement interface may be brittle

Methods of wetting enhancement

- Coat reinforcement with a metal (e.g., Ni, Cu, Ag) by plating
- Coat reinforcement with a ceramic (e.g., TiC, SiC, B₄C, TiB₂, TiN, K₂ZrF₆, ZrO₂) by CVD, solution coating, etc.

Coating of TiB $_2$ on carbon fiber by CVD

- TiCl₄ and BCl₃ gases, which are reduced by zinc vapor
- Coating particularly good for liquid aluminum

Solution coating method

- Dip in organometallic solution (e.g., alkoxides, which are M(OR)_x, where M is the metal, and R is a hydrocarbon group, such as methyl, ethyl, etc.)
- Hydrolysis or pyrolysis to organometallic compounds

Hydrolysis of organometallic compound

$$M(OR)_{x} + \frac{x}{2}H_{2}O \rightarrow MO_{x/2} + xROH$$

 $Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$

Pyrolysis of organometallic compound

$$\mathrm{Si}(\mathrm{OC}_{2}\mathrm{H}_{5})_{4} \rightarrow \mathrm{SiO}_{2} + 2\mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH} + 2\mathrm{C}_{2}\mathrm{H}_{4}$$

Powder metallurgy

- Near-net shape
- Size limited by the pressure requirement

Two methods of powder metallurgy

- Mixture of matrix powder and reinforcement particles/fibers
- Matrix coated reinforcement particles/fibers







Microstructure of tungsten carbide—20% cobaltcemented carbide (1300). (From Metals Handbook, Vol. 7, 8th Ed., American Society for Metals, 1972.)



Microstructure of an aluminum casting alloy reinforced with silicon carbide particles. In this case, the reinforcing particles have segregated to interdendritic regions of the casting (´ 125).





Ceramic-matrix composites

- Ceramic-ceramic composites (ceramic-fiber ceramic-matrix composites)
- Better oxidation resistance than carbon-carbon composites
- Technology less matured than carbon-carbon composite technology

Examples of ceramic matrices

- Silicon carbide
- Silicon nitride
- Alumina (aluminum oxide Al₂O₃)
- Mullite (Al₂O₃-SiO₂)
- Glasses