This talk deals with the description of the main fibers and matrices used in composite materials such as carbon, aramid and glass fibers and epoxy, vinyl ester and epoxy resins. The last part of the talk will be devoted to the ply properties of the T300/N5208 carbon/epoxy system.
A Fiber may be defined as an elongated stringy man-made material. The interior structure of carbon, aramid and glass fibers will be described in the first place. This is a key issue in terms of understanding how fibers work from a mechanical point of view. A polymer is a large molecule consisting of repeating units connected by covalent chemical bonds. Once the polymer is combined with the fibers, the polymerization process must take place in order to obtain a solid structural composite material. The polymerization mechanism of the epoxy matrix will be described by means of an animation. Another critical issue is the fiber-matrix bonding. When the composite material is loaded, both fibers and matrix must be strongly bonded so that they work as a solid rigid. The bonding mechanisms of carbon/epoxy and glass/epoxy systems will be described by means of animations.
Two parts may be distinguished in a fiber in terms of performance/processing: the **interior structure** and the **exterior surface**. The Young’s modulus of a unidirectional composite in the fiber direction depends mostly on the modulus of the fiber itself. However, other properties such as compression, transverse and shear strengths depend also on the fiber/matrix bonding, that will be studied later in this talk. The interior structure of the fiber is much related to its mechanical properties. For instance, the interior structure of the carbon fiber is composed of very strong covalent bonds between carbon atoms, which make this material one of the strongest and stiffest. Aramid fibers are composed of a crystalline polymer, an aromatic polyamide. In this case, the hydrogen bonds are the base for the mechanical performance of this fibers. Carbon and aramid are anisotropic fibers, in other words, present different properties in longitudinal and radial directions due to their oriented interior structures. Differently, glass in as isotropic material composed mostly of silica.
Carbon fibers present the highest tensile strengths and moduli, and also the lowest strains-to-failure. On the contrary, glass fibers are the most flexible, exhibiting the highest strains-to-failure. Aramid fibers present a tensile modulus lower than carbon and higher than glass.
Longitudinal versus transverse modulus of the fiber is shown in this slide. Organic fibers exhibit a high degree of anisotropy. PBO fibers have the highest longitudinal modulus and lowest transverse modulus among all organic fibers.

Inorganic fibers exhibit a variable degree of anisotropy: basalt and glass fibers have a longitudinal/transverse modulus ratio close to 1. However, carbon fibers are highly anisotropic.
Carbon fibers present outstanding fatigue and bonding with epoxy, their cost is high. It is used in aerospace and high performance applications.

Glass fibers have moderate strength and low cost. They present low stiffness. They are widely used in low-medium performance applications.

Basalt fibers have high chemical and alkali resistance, however they present limited bonding to polymers. Reinforcing concrete and infrastructure are typical applications.

Aramid fibers present great impact resistance and toughness. They have low compression strength. They are used in impact and ballistic applications.

HDPE fibers have high ballistic resistance, tensile strength and toughness. They have low compression strength. They are also used in impact and ballistic applications.

PBO fibers have excellent tensile strength and thermal stability. They are highly anisotropic and low fatigue resistant. Space, sporting goods and conductive textiles are typical applications.
Carbon fiber densities are low compared to metal and glass fibers: 1.8 – 2 g/cm³. Tensile strength is outstanding reaching 6 GPa for PAN based carbon fibers, while pitch based fibers range from 1.5 – 3 GPa. In terms of tensile modulus, pitch fibers reach 970 GPa, while PAN based fibers range 220-450 GPa. The conclusion of this Table is that carbon fiber is a leading material in terms of specific stiffness and strength.
There are two main precursors to produce carbon fibers: Polyacrylonitrile (PAN), obtained from propylene and ammonia and pitch obtainable during an oil refining process. The stabilization takes place at 500°C, the goal being the stretching of the fibers. The carbonization provokes the orientation and shrinking of the carbon fibers by increasing the temperature up to 1000-1500°C. Finally, the graphitization with temperatures ranging 2000-3000°C increases consistently the fiber modulus. Carbon fibers have a carbon content between 93-95% while graphite fibers have a carbon content higher than 99%.
Their main characteristics are: Anisotropic fibers, with diameters 6-12 μm. Excellent fatigue behavior. Low thermal expansion, may be negative. Adjacent metals corrode due to galvanic coupling. Low impact resistance. Brittleness. Low strains to failure. Surface must be treated. High cost. Their outstanding tensile strength and modulus are due to the strong covalent bonds between carbon atoms. Radially, the most oriented structure is located in the exterior area. When increasing the treatment temperature through the carbonization and graphitization processes, the modulus increases because of the higher fraction of carbon atoms and because the crystal is increasingly oriented in the fiber direction.
There are mainly three types of glass fibers:

**S-glass**: high performance, high cost (helicopter blades, ballistic armor, windsurfers,…)

**E-glass**: the most used, moderate mechanical properties (industrial applications)

**AR-glass**: is used in concrete/cement matrix composite structures such as infrastructure.

S-glass shows the greatest strength due to the fact that its composition close to that of the SiO2-Al2O3-MgO is eutectic under particular conditions of drawing. Fibers of borate, such as E-glass present weaker structural bonds.

The main characteristic of glass fiber is the high tensile strength, which ranges from 3.1 to 4.6 Gpa.

**Basalt fibers** are inexpensive, golden brown-colored fibers and similar to glass. Basalt exhibits better chemical and alkali resistance than glass, promising an additional choice for use in reinforcing concrete in infrastructure applications.
Fiberglass manufacturing starts from the furnace at 1250 °C, then the molten material flows into a fore-hearth. The molten material is gravity-fed from the fore-hearth at each forming position into a platinum alloy “bushing”. Electricity is passed through the bushing to provide a final stage of resistance heating and precise adjustment of the viscosity of the molten mixture. Each bushing has hundreds of micro-holes each make a filament that is gathered into a single strand of continuous-filament glass fiber.

The combination of micro-hole size and viscosity of the melt determine the diameter of the resulting filaments (10-20μ). The glass filaments are quenched with a water-based sizing to solidify the strands and deposit a small quantity of lubricant/bonding agent on the filaments.

The strands are wound onto a bobbin called a forming package at high speed. The strands can then be sold as an untwisted roving, twisted/plied into a yarn for weaving, or chopped to a fixed length for production of a non-woven mat.
Iberglass is a uniform material of arguable phase, produced when the viscous molten material cools very rapidly to below its glass transition temperature, without sufficient time for a regular crystal lattice to form. Their main characteristics are: Isotropic fibers with diameters 10 - 20 μm. Moderate tensile strength. High impact resistance. High strain-to-failure. Low tensile modulus. Poor fatigue behavior compared to carbon. Good chemical resistance. Transparent to electromagnetic waves. Good adhesion with polymeric matrices. Good fire behavior. Thermal insulation. Low dielectric. Low cost.
Basalt fibers are made by melting a single material, basalt rock. The manufacturing process is very similar to glass.

They present high tensile modulus and strength, but poor bonding to polymers.

Basalt fiber composites are less stiff and strong than E-Glass due to poor interfacial strength.
Basalt fiber present a outstanding chemical resistance. After three hours boiling in a saturated boiling solution, the weight loss is lower than AR-glass fibers. E-glass shows much worse behavior than AR-glass and basalt fibers.

After four weeks at 50°C in a highly alkaline solution, SEMS shows the best surface for basalt, AR-glass are lightly affected and E-glass surface is much deteriorated.
HDPE is the lightest organic fiber compared to aramid and PBO.

PBO fibers are the stiffest and strongest. These fibers show also the highest elongation to failure.

Aramid fibers exhibit the lowest coefficient of thermal expansion.
Aramid is an aromatic polyamide, therefore aramid fibers are organic. Their main characteristics are: Anisotropic fibers with diameters of 12 μm. Excellent toughness. Outstanding ballistic and impact resistance. High tensile strength due to highly oriented molecular chains. Poor adhesion to the matrix. Low thermal expansion, may be negative. Transparent to electromagnetic waves. Absorb moisture (hygroscopic). Low maximum temperature of operation: 175°C. Difficult to machine. Poor fire behavior. High cost. By means of a bright synchrotron radiation and a special type of x-ray microscopy, called xanes, the secret internal structure of aramid fiber were revealed in 2002.

The repeat unit of Kevlar is shown on the left. This is monoclinic primary structure. The secondary structure consists of pleated crystalline sheets radially arranged. These pleats are induced by stress relaxation during coagulation. On the one hand, this secondary structure creates the nearly perfect orientation of the fiber, but the existence of microvoids and other defects around the periphery of the fiber prevent the orientation from being truly perfect. On the other hand, Aramid fibers exhibit strong covalent bonding in the fiber direction and weak hydrogen bonding in the transverse direction. In other words, the stacking sheets form a crystalline array, but between the sheets the bonding is weak. These are the two main reasons for the low and ductile compression strength of organic fibers. The longitudinally strong array of plates and the low strength/ductile failure exhibited in the transverse direction are also the key reasons for the high impact and toughness.
**Ultrahigh Molecular Weight Polyethylene fibers**

These fibers have excellent toughness, outstanding ballistic and impact resistance and high tensile strength due to highly oriented molecular chains. However, they have poor compression strength due to lack of adhesion to the matrix.

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Polarized Light Microscopy Digital Image shows a highly oriented linear molecular chain and spoke-like cross section.
PBO are currently the highest tensile modulus, highest tensile strength, and most thermally stable commercial polymeric fibers. This is due to the high linear crissallinity of the structure.

However, PBO has low axial compressive strength and poor resistance to ultraviolet and visible radiation. The fiber also loses tensile strength in hot and humid environment.

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However, PBO has low axial compressive strength and poor resistance to ultraviolet and visible radiation. The fiber also loses tensile strength in hot and humid environment.
1. What are the two phenomena that make the carbon fiber stiffer when increasing the treatment temperature through carbonization and graphitization?

2. What makes the aramid fibers so strong in toughness and tension and so weak in compression?

3. What makes S-Glass stronger than E-Glas?
THERMOSET MATRICES
The toughness limitation of thermoset matrices is a direct result of their rigid, highly-cross linked, glassy polymer structures that form during cure. These rigid structures have high-temperature capability and the ability of the rigid matrix to stabilize the fibers during compression loading but they develop susceptibility to delaminations when impacted. Currently there are attempts to use molecular dynamics to predict gross properties of matrix. So far they have not been successful for several reasons, such as:

1) modeling of cross linking of matrix is very complicated as compared with uncross linked matrix;
2) work for deformation is attainable but for failure is hopeless because defects will control the failure process. To model defects is not possible unless many empirical constants are used or use reverse engineering.
Epoxies are the most used matrices for high-performance composites. They exhibit high fatigue strength, excellent adhesion to fibers, low shrinkage (about 2%) and processing versatility. In areas that must be able to flex and strain with the fibers without micro-fracturing, epoxy resins offer much greater capability. Cured epoxy tends to be very resistant to moisture absorption. Epoxy resin will bond dissimilar or already-cured materials which makes repair work that is reliable and strong.

The epoxy group is extremely efficient in terms of bonding to almost any kind of material.

<table>
<thead>
<tr>
<th>Thermoset matrices</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>epoxy group:</td>
<td><img src="image" alt="Epoxy Group" /></td>
</tr>
</tbody>
</table>
The curing mechanism is composed of the following phases:

1) The resin containing diepoxy prepolymer is applied
2) The hardener—usually a diamine—is added
3) One hydrogen atom from the diamine reacts with the oxygen atom from the epoxy group
4) This reaction occurs as well with other epoxide groups near the diamine
5) All the diamines react in a similar way, crosslinking the diepoxy prepolymer and polymerizing the epoxy
6) The prepolymer and the diamines bond strongly between them forming a three-dimensional network
Vinyl esters are similar to polyesters but have only reactive groups at the end of the molecular chain. Due to this lower cross link density, they are tougher than polyesters. They use the same catalysts and accelerators as polyester. Vinyl esters are presented in solutions with 30-40% of styrene. These resins offer as well water and corrosion resistance. These enhanced properties are obtained without complex processing, handling or special shop fabricating practices that are typical with epoxy resins. They also exhibit good heat retardance properties when brominated and shrinkage during curing (about 7%). Differently to polyesters, the ester groups are at the end of the molecular chains. Since these groups are susceptible to hydrolysis by water, vinyl esters are more resistant to degradation from water/moisture. Similarly, the links are also at the end of the molecular chains. Due to this lower cross link density, vinyl esters are tougher than polyesters.
Polyesters are viscous liquids consisting of a solution of polyester in a monomer, usually styrene, which is the cross-linking agent. The polyester contains ester groups and unsaturated or double-bond reactive groups. The styrene is the cross-linking agent. An initiator, usually a peroxide, is required to start the reaction between the polyester and the styrene. The result is a rigid cross-linked structure, with many reactive points (brittleness) and many ester groups (susceptible to hydrolysis by water). Extensively used in commercial low-performance applications. May be formulated at room temperature or elevated temperatures. However, non adequate for advanced composites due to: Low temperature capability, low weathering resistance, exhibit shrinkage during curing (about 7%), environment problems due to presence of styrene, low toughness, poor adhesion to carbon and aramid.
After 7 days curing at 20C, epoxy exhibits the highest tensile strength, 22% superior to vinyl ester and polyester. Curing at 5 hours at 80C increases the tensile strength from 60 to 80 MPa, vinyl ester and polyester tensile strengths also increase from 48 to 75 MPa (vinyl ester) and from 48 to 62 (polyester).
The tensile modulus for epoxy is higher than vinyl ester and polyester. For curing 7 days at 20°C, the epoxy modulus is 3.4 GPa, a little bit higher than curing at 5 hours at 80°C. Tensile moduli for vinyl ester and polyester range from 2 to 3 MPa.
The strain to failure for epoxy is around 7%, while vinyl ester and polyester exhibit strain-to-failure values of 4.5 and 3% respectively.
Left: Epoxy is more fatigue resistant than vinyl ester and epoxy, specially when combined with carbon fibers (S-N curves)

Right: Prof. Miyano will introduce the accelerated testing methodology. Fatigue strength master curves are shown. They were constructed using test data and shift factor for the matrix resin. This figure shows the tensile strength versus reduced time to failure on the lower horizontal axis, and at reduced temperature at the upper horizontal axis. The parameter of various load cycles Nf is shown.
Phenolic resins are used when fire and smoke requirements are present. Typical applications are aircraft and rail interiors, or marine constructions. This thermoset resin is produced by the condensation of an aromatic alcohol with an aldehyde such as phenol with formaldehyde. Phenolic resin composites are not as structural as epoxy resin ones due to the lower Young’s modulus and tensile strength of the resultant composite materials.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>1.28 - 2.13</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>4.1 – 8.2</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>53.5 – 60</td>
</tr>
<tr>
<td>Strain to failure (%)</td>
<td>0.72 - 2</td>
</tr>
<tr>
<td>Mold shrinkage (mm/mm)</td>
<td>0.005 to 0.010</td>
</tr>
<tr>
<td>Max. processing Temperature (°C)</td>
<td>170</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.03 - 0.35</td>
</tr>
</tbody>
</table>

Phenolic resins are used when fire and smoke requirements are present. Typical applications are aircraft and rail interiors, or marine constructions. This thermoset resin is produced by the condensation of an aromatic alcohol with an aldehyde such as phenol with formaldehyde. Phenolic resin composites are not as structural as epoxy resin ones due to the lower Young’s modulus and tensile strength of the resultant composite materials.
These high temperature resins with Tg around 220°C are used high performance structural composites requiring higher temperature use and increased toughness. They can be processed at the same temperature (175°C) and pressure (0.69 MPa) as epoxies. Autoclave curing, filament winding and RTM may be used for processing. Their tack and drape are quite good due to the liquid nature of the reactants. Degradation of the polymer may happen when combined with carbon fiber due to a galvanic couple.

### Properties of bismaleimide resins

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.23</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>2.7 – 3.5</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>45</td>
</tr>
<tr>
<td>Strain to failure (%)</td>
<td>1.3 – 2.2</td>
</tr>
<tr>
<td>HDT (°C)</td>
<td>230</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>1.7 – 3.7</td>
</tr>
</tbody>
</table>
These resins may be used as high as 315°C and are more difficult to process than epoxies of BMIs, because they require 370°C and 1.38 MPa as processing T and P. Working at such high temperatures leads to challenging problems such as poor track and drape, difficulty to produce thick laminates, tendency towards microcracking and management of volatiles and voids during curing.

Space applications are the most common for this resin due to its characteristics and high cost.
1. What makes epoxy apt to be bonded to almost any kind of material?

2. Why vinyl ester is increasingly used in medium performance applications (give four reasons)?

3. Why polyester is not used in high performance applications (give two reasons?)
FIBER-MATRIX BONDING
Carbon bonds well with epoxy (oxidizing agents) while aramid surface is not chemically active and glass bonds with all polymers by means of organosilanes. The highest interfacial shear strength reported corresponds to carbon/epoxy (86 MPa). The second highest interfacial shear strength is for glass/epoxy (56 MPa), the rest of the bonds present modest shear strength values.
There are four main bonding mechanisms present in organic matrix composite materials:

**Covalent bonding.** The strongest, two or more electrons are shared (the most common in composite materials)

**Electrostatic attraction.** Key is surface charge density (Van der Waals, 1/10 of covalent forces)

**Molecular entanglement.** Molecular conformation structure (fibers precoated with polymers)

**Mechanical adhesion.** Key is roughness (fiber/concrete)
The non-polarity of carbon fiber surface results in poor chemical bonding with a resin matrix, and the smooth surface leads to a reduction of mechanical interlocking. The major method is the liquid-phase oxidative treatment which is done by drawing the fibers through a bath of some oxidizing agents such as nitric acid, potassium permanganate, or sodium hypochlorite, or through an acidic or alkaline electrolytic bath. The gradual increase of surface roughness on oxygen-treated fibers promotes more mechanical keying as well as functional groups (carboxyl, carbonyl and hydroxyl) which enhances the interfacial bonding between the fibers and the resin.
Because of high crystallinity, the surface of aramid fibers is chemically inert and smooth, thus its adhesion with the resin matrix is poor. Therefore, surface modification is essential to enhance its reinforcing effect. There are three approaches of surface-modification for aramid fibers:

a) Coating with coupling agents or physical, chemical treatment to form chemical bonding with resins on the surface of the fiber

b) Roughening the surface of the fiber to enlarge the physical interface with the resin matrix and thus effects of the mechanical anchoring

c) Chemical activation of the surface of the fiber
After melting the glass at 1250 °C, and being humidified, the filaments contain silanol groups.

Sizings (1-2% by weight) are thin coatings, usually organosilane coupling agents with the structure $X_3SiR$, which in presence of water, form silanol groups.

Then condense with the silanol groups at the surface of the glass fibers to form siloxanes, where the $R$ group will react with the polymeric matrix.
These photomicrographs of glass beads in polyamide demonstrate the effectiveness of *silane* treatment in providing intimate filler-matrix contact. In addition to facilitating stress transfer, this minimizes or eliminates voids at the filler-matrix interface where moisture or gases can penetrate.
1. What is the best treatment for carbon fiber in order to get a good bonding to polymers?

2. Why aramid-polyester is not used at all for structural applications?

3. What is the best treatment for glass fiber in order to get a good bonding to polymers?
The main applications of composite materials are composed of **carbon/epoxy** (high performance applications), **glass/epoxy** (typical material in large wind turbine blades) and **glass/polyester** due to its low cost. The fiber T700-F0E has improved lightly the interphase properties of **carbon/vinyl ester** with respect to regular T700 fibers. **Aramid/epoxy** is used for impact applications among others. **Glass** bonds well with epoxy, vinyl ester and polyester.
PLY PROPERTIES
Stiffness ply properties are the following:

$E_x$, Young’s Modulus in the fiber direction

$E_y$, Young’s Modulus in the transverse direction

$\nu_x$, Major Poisson’s Ratio

$\nu_x = \frac{-E_y}{E_x}$

$E_s$, In-plane Shear Modulus

$\nu_x$, Poisson’s Ratio

$E_s$, In-plane Shear Modulus
Strength ply properties are the following:

X, Tensile Strength in x
X’, Compression Strength in x
Y, Tensile Strength in y
Y’, Compression Strength in y
S, In-plane Shear Strength
T300/N5208 Carbon/Epoxy

**Stiffness Data**

- $E_x = 181$ GPa, 26.25 msi
- $E_y = 10.3$ GPa, 1.49 msi
- $v_x = 0.28$
- $v_x = -v_y / v_x$
- $E_s = 7.17$ GPa, 1.04 msi

$Ex = 181$ GPa, 26.25 msi
$Ey = 10.3$ GPa, 1.49 msi
$\mu_x = 0.28$
$Es = 7.17$ GPa, 1.04 msi
T300/N5208 Carbon/Epoxy

Strength Data

X = 1500 MPa, 217.5 ksi
X' = 1500 MPa, 217.5 ksi
Y = 40 MPa, 5.8 ksi
Y' = 246 MPa, 35.67 ksi
S = 68 MPa, 9.86 ksi