RUBBER PROCESSING
TECHNOLOGY

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Overview of Rubber Processing

- Many of the production methods used for plastics are also applicable to rubbers
- However, rubber processing technology is different in certain respects, and the rubber industry is largely separate from the plastics industry
- The rubber industry and goods made of rubber are dominated by one product: tires
  - Tires are used in large numbers on automobiles, trucks, aircraft, and bicycles
Two Basic Steps in Rubber Goods Production

1. Production of the rubber itself
   - Natural rubber (NR) is an agricultural crop
   - Synthetic rubbers is based on petroleum

2. Processing into finished goods:
   - Compounding
   - Mixing
   - Shaping
   - Vulcanizing

The Rubber Industries

- Production of raw NR is an agricultural industry because latex, the starting ingredient, is grown on plantations in tropical climates
- By contrast, synthetic rubbers are produced by the petrochemical industry
- Finally, processing into tires and other products occurs at processor (fabricator) plants, commonly known as the rubber industry
Production of Natural Rubber

- Natural rubber is tapped from rubber trees (*Hevea brasiliensis*) as latex
  - In Southeast Asia and other parts of the world
- Latex is a colloidal dispersion of solid particles of the polymer *polyisoprene* in water
  - Polyisoprene (C$_5$H$_8$)$_n$ is the chemical substance that comprises NR, and its content in the emulsion is about 30%

Recovering the Rubber

- Preferred method to recover rubber from latex involves coagulation - adding an acid such as formic acid (HCOOH)
  - Coagulation takes about 12 hours
- The coagulum, now soft solid slabs, is then squeezed through rolls which drive out most of the water and reduce thickness to about 3 mm (1/8 in)
- The sheets are then draped over wooden frames and dried in smokehouses for several days
Grades of Natural Rubber

- The resulting rubber, now in a form called *ribbed smoked sheet*, is folded into large bales for shipment to the processor.
- In some cases, the sheets are dried in hot air rather than smokehouses, and the term *air-dried sheet* is used.
  - This is considered a better grade of rubber.
- A still better grade, called *pale crepe* rubber, involves two coagulation steps, followed by warm air drying.

Synthetic Rubber

- Most synthetic rubbers are produced from petroleum by the same polymerization techniques used to synthesize other polymers.
- Unlike thermoplastic and thermosetting polymers, which are normally supplied to the fabricator as pellets or liquid resins, synthetic rubbers are supplied to rubber processors in the form of large bales.
  - The rubber industry has a long tradition of handling NR in these unit loads.
Compounding

- Rubber is always compounded with additives
  - Compounding adds chemicals for vulcanization, such as sulfur
  - Additives include fillers that either enhance the rubber's mechanical properties (reinforcing fillers) or extend the rubber to reduce cost (non-reinforcing fillers)
  - It is through compounding that the specific rubber is designed to satisfy a given application in terms of properties, cost, and processability

Carbon Black in Rubber

- The single most important reinforcing filler in rubber is carbon black, a colloidal form of carbon obtained by thermal decomposition of hydrocarbons (soot)
  - It increases tensile strength and resistance to abrasion and tearing of the final rubber product
  - Carbon black also provides protection from ultraviolet radiation
  - Most rubber parts are black in color because of their carbon black content
Other Fillers and Additives in Rubber

- China clays - hydrous aluminum silicates ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) reinforce less than carbon black but are used when the color black is not acceptable
- Other polymers, such as styrene, PVC, and phenolics
- Recycled rubber added in some rubber products, but usually 10% or less
- Antioxidants; fatigue- and ozone-protective chemicals; coloring pigments; plasticizers and softening oils; blowing agents in the production of foamed rubber; mold release compounds

Mixing

- The additives must be thoroughly mixed with the base rubber to achieve uniform dispersion of ingredients
- Uncured rubbers have high viscosity so mechanical working of the rubber can increase its temperature up to 150°C (300°F)
- If vulcanizing agents were present from the start of mixing, premature vulcanization would result - the “rubber processor’s nightmare”
Mixers in Rubber Processing

- (a) Two-roll mill and
- (b) Banbury-type internal mixer

Two-Stage Mixing

To avoid premature vulcanization, a two-stage mixing process is usually employed

- Stage 1 - carbon black and other non-vulcanizing additives are combined with the raw rubber
  - This stage 1 mixture is called the master batch
- Stage 2 - after stage 1 mixing is completed, and cooling time has been allowed, stage 2 mixing is carried out in which vulcanizing agents are added
Filament Reinforcement in Rubber

- Many products require filament reinforcement to reduce extensibility but retain the other desirable properties
  - Examples: tires, conveyor belts
  - Filaments include cellulose, nylon, and polyester
  - Fiber-glass and steel are also used (e.g., steel-belted radial tires)
  - Continuous fiber materials must be added during shaping; they are not mixed like the other additives

Shaping and Related Processes for Rubber Products

- Four basic categories of shaping processes:
  1. Extrusion
  2. Calendering
  3. Coating
  4. Molding and casting
- Some products require several basic processes plus assembly work (e.g., tires)
Extrusion

- Screw extruders are generally used
- The L/D ratio of the extruder barrel is less than for thermoplastics
  - Typical range 10 to 15
  - Reduces risk of premature cross-linking
- Die swell occurs in rubber extrudates
  - The highly plastic polymer exhibits “memory”
  - The rubber has not yet been vulcanized

Calendering

Rubber stock is passed through a series of gaps of decreasing size by a stand of rotating rolls
- Rubber sheet thickness is slightly greater than final roll gap due to die swell
Roller Die Process

Combination of extrusion and calendering that results in better quality product than either extrusion or calendering alone.

Coating or Impregnating Fabrics with Rubber

- Important industrial process for producing tires, conveyor belts, inflatable rafts, and waterproof cloth.
Molded Rubber Products

- Molded rubber products include shoe soles and heals, gaskets and seals, suction cups, and bottle stops
- Also, many foamed rubber parts are produced by molding
- In addition, molding is an important process in tire production

Molding Processes for Rubber

- Principal molding processes for rubber are
  1. Compression molding
  2. Transfer molding
  3. Injection molding
- Compression molding is the most important because of its use in tire manufacture
Molding Processes for Rubber

- Curing (vulcanizing) is accomplished in the mold in all three molding processes
  - This represents a departure from previous shaping methods
    - Other shaping methods use a separate vulcanizing step

What is Vulcanization?

The treatment that accomplishes cross-linking of elastomer molecules

- Makes the rubber stiffer and stronger but retain extensibility
- The long-chain molecules become joined at certain tie points, which is reduces the ability to flow
  - Soft rubber has 1 or 2 cross-links per 1000 mers
  - As the number of cross-links increases, the polymer becomes stiffer (e.g., hard rubber)
Effect of Vulcanization on Rubber Molecules

(1) raw rubber, and (2) Vulcanized (cross-linked) rubber: (a) soft rubber and (b) hard rubber


Vulcanization Chemicals and Times

- When first invented by Goodyear in 1839, vulcanization used sulfur (about 8 parts by weight of S mixed with 100 parts of NR) at 140°C (280°F) for about 5 hours
  - Vulcanization with sulfur alone is no longer used, due to long curing times
- Various other chemicals (e.g., zinc oxide, stearic acid) are combined with smaller doses of sulfur to accelerate and strengthen the treatment
  - Resulting cure time is 15-20 minutes

Tires and Other Rubber Products

- Tires are about 75% of total rubber tonnage
- Other important products:
  - Footwear
  - Seals
  - Shock-absorbing parts
  - Conveyor belts
  - Hose
  - Foamed rubber products
  - Sports equipment

Pneumatic Tires

- Functions of pneumatic tires on vehicle:
  - Support the weight of the vehicle, passengers, and cargo
  - Transmit the motor torque to propel the vehicle
  - Absorb road vibrations and shock to provide a comfortable ride
  - Tires are used on automobiles, trucks, buses, farm tractors, earth moving equipment, military vehicles, bicycles, motorcycles, and aircraft
Tire Construction

- A tire is an assembly of many components
  - About 50 for a passenger car tire
  - Large earthmover tire has as many as 175
- The internal structure of the tire, known as the carcass, consists of multiple layers of rubber-coated cords, called plies
  - The cords are strands of nylon, polyester, fiber glass, or steel, which provide inextensibility to reinforce the rubber in the carcass

Three Tire constructions: (a) diagonal ply, (b) belted bias, and (c) radial ply
Tire Production Sequence

- Tire production is summarized in three steps:
  1. Preforming of components
  2. Building the carcass and adding rubber strips to form the sidewalls and treads
  3. Molding and curing the components into one integral piece
- Variations exist in processing depending on construction, tire size, and type of vehicle

Preforming of Components

- Carcass consists of multiple components, most of which are rubber or reinforced rubber
- These components and others are produced by continuous processes
  - They are then pre-cut to size and shape for subsequent assembly
  - Other components include: bead coil, plies, inner lining, belts, tread, and sidewall
Building the Carcass

- Prior to molding and curing, the carcass is assembled on a building drum, whose main element is a cylindrical arbor that rotates.

Molding and Curing

- (1) Uncured tire placed over expandable diaphragm, (2) split mold is closed and diaphragm is expanded to force uncured rubber against cavity with tread pattern; mold & diaphragm are heated to cure rubber.
Other Rubber Products: Rubber Belts

- Widely used in conveyors and pulley systems
- Rubber is ideal for these products due to its flexibility, but the belt must have little or no extensibility
  - Accordingly, it is reinforced with fibers, commonly polyester or nylon
- Fabrics of these polymers are usually coated by calendering, assembled together to obtain required number of plies and thickness, and subsequently vulcanized by continuous or batch heating processes

Other Rubber Products: Hose

Two basic types:
1. Plain hose (no reinforcement) is extruded tubing
2. Reinforced tube, which consists of:
   - Inner tube - extruded of a rubber compounded for particular liquid that will flow through it
   - Reinforcement layer - applied to inner tube as fabric, or by spiraling, knitting, braiding
   - Outer layer – compounded for environment and applied by extrusion
Other Rubber Products: Footwear

- Rubber components in footwear: soles, heels, rubber overshoes, and certain upper parts
- Molded parts are produced by injection molding, compression molding, and certain special molding techniques developed by the shoe industry
- The rubbers include both solid and foamed
- For low volume production, manual methods are sometimes used to cut rubber from flat stock

Processing of Thermoplastic Elastomers

A thermoplastic elastomer (TPE) is a thermoplastic polymer that possesses the properties of a rubber

- TPEs are processed like thermoplastics, but their applications are those of an elastomer
- Most common shaping processes are injection molding and extrusion
  - Generally more economical and faster than the traditional processes for rubbers that must be vulcanized
TPE Products

- Molded products: shoe soles, athletic footwear, and automotive components such as fender extensions and corner panels
- Extruded items: insulation coating for electrical wire, tubing for medical applications, conveyor belts, sheet and film stock
- No tires of TPE

Product Design Considerations

Economic Production Quantities:

- Rubber parts produced by compression molding (the traditional process) can often be produced in quantities of 1000 or less
  - The mold cost is relatively low compared to other molding methods
- As with plastic parts, injection molding of rubber parts requires higher production quantities to justify the more expensive mold
Product Design Considerations

Draft:
- Draft is usually unnecessary for molded parts of rubber, because its flexibility allows it to deform for removal from the mold
- Shallow undercuts, although undesirable, are possible with rubber molded parts for the same reason
- The low stiffness and high elasticity of the material permits removal from the mold

Overview of PMC Technology

A polymer matrix composite (PMC) is a composite material consisting of a polymer imbedded with a reinforcing phase such as fibers or powders
- PMC processes are important due to the growing use of PMCs, especially fiber-reinforced polymers (FRPs)
  - FRP composites can be designed with very high strength-to-weight and modulus-to-weight ratios
  - These features make them attractive in aircraft, cars, trucks, boats, and sports equipment
Many PMC shaping processes are slow and labor intensive

In general, techniques for shaping composites are less efficient than for other materials - Why?
- Composites are more complex than other materials
- Need to orient the reinforcing phase in FRPs
- Composite processing technologies have not been the object of refinement over as many years as processes for other materials

Categories of FRP Shaping Processes

- Open mold processes - Based on FRP manual procedures for laying resins and fibers onto forms
- Closed mold processes - similar to plastics molding
- Filament winding - continuous filaments are dipped in liquid resin and wrapped around a rotating mandrel, producing a rigid, hollow, cylindrical shape
- Pultrusion - similar to extrusion only adapted to include continuous fiber reinforcement
- Other - operations not in previous categories
Classification of manufacturing processes for fiber reinforced polymer (FRP) composites

Starting Materials for PMCs

- In a PMC, the starting materials are:
  - A polymer
  - A reinforcing phase
  - They are processed separately before becoming phases in the composite
Polymer Matrix

- Thermosetting (TS) polymers are the most common matrix materials
  - Principal TS polymers are:
    - Phenolics – particulate reinforcing phases
    - Polyesters and epoxies - mostly FRPs
  - Thermoplastic molding compounds include fillers or reinforcing agents
  - Nearly all rubbers are reinforced with carbon black

Reinforcing Agent

- Possible materials - ceramics, metals, other polymers, or elements such as carbon or boron
- Possible geometries - fibers, particles, and flakes
  - Particles and flakes are used in many plastic molding compounds
  - Of most engineering interest is the use of fibers as the reinforcing phase in FRPs
Fibers as the Reinforcing Phase

- Common fiber materials: glass, carbon, and Kevlar
- In some fabrication processes, the filaments are continuous, while in others, they are chopped into short lengths
  - In continuous form, individual filaments are usually available as *roving* - collections of untwisted continuous strands, convenient form for handling
  - By contrast, a *yarn* is a twisted collection of filaments


Fibers as the Reinforcing Phase

- The most familiar form of continuous fiber is a *cloth* - a fabric of woven yarns
- A *woven roving* is similar to a cloth, but it consists of untwisted filaments rather than yarns
  - Woven rovings can be produced with unequal numbers of strands in the two directions so that they possess greater strength in one direction
    - Such unidirectional woven rovings are often preferred in laminated FRP composites

Mats and Preforms as Reinforcements

- Fibers can also be in a mat form - a felt consisting of randomly oriented short fibers held loosely together with a binder
  - Mats are commercially available as blankets of various weights, thicknesses, and widths
  - Mats can be cut and shaped for use as preforms in some of the closed mold processes
  - During molding, the resin impregnates the preform and then cures, thus yielding a fiber-reinforced part

Combining Matrix and Reinforcement: Two Approaches

1. The starting materials arrive at the fabrication operation as separate entities and are combined into the composite during shaping
   - Filament winding and pultrusion, in which reinforcing phase = continuous fibers
2. The two component materials are combined into some starting form that is convenient for use in the shaping process
   - Molding compounds
   - Prepregs
Molding Compounds

FRP composite molding compounds consist of the resin matrix with short randomly dispersed fibers, similar to those used in plastic molding:

- Most molding compounds for composite processing are thermosetting polymers
- Since they are designed for molding, they must be capable of flowing
  - They are not cured prior to shape processing
  - Curing is done during and/or after final shaping

Process for Producing Sheet Molding Compound (SMC)
Prepregs

Fibers impregnated with partially cured TS resins to facilitate shape processing

- Available as tapes or cross-plied sheets or fabrics
- Curing is completed during and/or after shaping
- Advantage: prepregs are fabricated with continuous filaments rather than chopped random fibers, thus increasing strength and modulus

Open Mold Processes

Family of FRP shaping processes that use a single positive or negative mold surface to produce laminated FRP structures

- Starting materials (resins, fibers, mats, and woven rovings) are applied to the mold in layers, building up to the desired thickness
- This is followed by curing and part removal
- Common resins are unsaturated polyesters and epoxies, using fiberglass as the reinforcement
Open Mold FRP Processes

1. Hand lay-up
2. Spray-up
3. Automated tape-laying machines
   - The differences are in the methods of applying the laminations to the mold, alternative curing techniques, and other differences.

Hand Lay-Up Method

Open mold shaping method in which successive layers of resin and reinforcement are manually applied to an open mold to build the laminated FRP composite structure

- Labor-intensive
- Finished molding must usually be trimmed with a power saw to size outside edges
- Oldest open mold method for FRP laminates, dating to the 1940s when it was first used for boat hulls.
Hand Lay-Up Method

- (1) mold is treated with mold release agent; (2) thin gel coat (resin) is applied to outside surface of mold; (3) when gel coat has partially set, layers of resin and fiber mat or cloth are applied, each layer is rolled to impregnate the fiber with resin and remove air

- (4) Part is cured; (5) fully hardened part is removed from mold
Products Made by Hand Lay-Up

- Generally large in size but low in production quantity - not economical for high production
- Applications: boat hulls, swimming pools, large container tanks, movie and stage props, and other formed sheets
- Largest molding ever made was ship hulls for the British Royal Navy: 85 m (280 ft) long

Spray-Up Method

Liquid resin and chopped fibers are sprayed onto an open mold to build successive FRP laminations
- Attempt to mechanize application of resin-fiber layers and reduce lay-up time
- Alternative for step (3) in the hand lay-up procedure
- Products: boat hulls, bathtubs, shower stalls, truck body parts, furniture, structural panels, containers
- Since products have randomly oriented short fibers, they are not as strong as those made by lay-up, in which the fibers are continuous and directed
**Spray-Up Method**

Machines that operate by dispensing a prepreg tape onto an open mold following a programmed path

- Typical machine consists of overhead gantry to which the dispensing head is attached
- The gantry permits x-y-z travel of the head, for positioning and following a defined continuous path
Automated Tape-Laying Machine

Curing in Open Mold Processes

- Curing is required of all thermosetting resins used in FRP laminated composites
- Curing cross-links the polymer, transforming it from its liquid or highly plastic state into a solid product
- Three principal process parameters in curing:
  1. Time
  2. Temperature
  3. Pressure
Curing at Room Temperature

- Curing normally occurs at room temperature for the TS resins used in hand lay-up and spray-up procedures
  - Moldings made by these processes are often large (e.g., boat hulls), and heating would be difficult due to product size
  - In some cases, days are required before room temperature curing is sufficiently complete to remove the part

Several Curing Methods Based on Heating

- Oven curing provides heat at closely controlled temperatures; some curing ovens are equipped to draw a partial vacuum
- Infrared heating - used in applications where it is impractical to place molding in oven
- Curing in an autoclave, an enclosed chamber equipped to apply heat and/or pressure at controlled levels
  - In FRP composites processing, it is usually a large horizontal cylinder with doors at either end
Closed Mold Processes

- Performed in molds consisting of two sections that open and close each molding cycle
- Tooling cost is more than twice the cost of a comparable open mold due to the more complex equipment required in these processes
- Advantages of a closed mold are: (1) good finish on all part surfaces, (2) higher production rates, (3) closer control over tolerances, and (4) more complex three-dimensional shapes are possible

Classification of Closed Mold Processes

- Three categories based on their counterparts in conventional plastic molding:
  1. Compression molding
  2. Transfer molding
  3. Injection molding
- The terminology is often different when polymer matrix composites are molded
Compression Molding PMC Processes

Charge is placed in lower mold section, and the mold sections are brought together under pressure, forcing charge to take the shape of the cavity

- Mold halves are heated to cure TS polymer
  - When molding is sufficiently cured, mold is opened and part is removed
- Several shaping processes for PMCs based on compression molding
  - The differences are mostly in the form of the starting materials

Transfer Molding PMC Processes

Charge of thermosetting resin with short fibers is placed in a pot or chamber, heated, and squeezed by ram action into one or more mold cavities

- Mold is heated to cure the resin
- The name of the process derives from the fact that the fluid polymer is transferred from a pot into a mold
Injection Molding PMC Processes

- Injection molding is noted for low cost production of plastic parts in large quantities
- Although most closely associated with thermoplastics, the process can also be adapted to thermosets
- Processes of interest in the context of PMCs:
  - Conventional injection molding
  - Reinforced reaction injection molding

Conventional Injection Molding

- Used for both TP and TS type FRPs
- Virtually all TPs can be reinforced with fibers
- Chopped fibers must be used
  - Continuous fibers would be reduced by the action of the rotating screw in the barrel
- During injection into the mold cavity, fibers tend to become aligned as they pass through the nozzle
- Part designers can sometimes exploit this to optimize directional properties in the part

Reinforced Reaction Injection Molding

Conventional *Reaction injection molding* (RIM) - two reactive ingredients are mixed and injected into a mold cavity where curing and solidification occur.

*Reinforced reaction injection molding* (RRIM) - similar to RIM but includes reinforcing fibers, typically glass fibers.

- Advantages: similar to RIM (no heat energy required, lower cost mold), but with fiber-reinforcement.
- Products: auto body and truck body parts.

Filament Winding

Resin-impregnated continuous fibers are wrapped around a rotating mandrel that has the internal shape of the desired FRP product.

- Resin is then cured and the mandrel removed.
- Fiber rovings are pulled through a resin bath before being wound in a helical pattern around the mandrel.
- The operation is repeated to form additional layers, each having a crisscross pattern with the previous, until the desired part thickness has been obtained.
Filament Winding

Filament Winding Machine
Pultrusion Processes

Similar to extrusion (hence the name similarity) but workpiece is pulled through die (so prefix "pul-" in place of "ex-")

- Like extrusion, pultrusion produces continuous straight sections of constant cross section
- Developed around 1950 for making fishing rods of glass fiber reinforced polymer (GFRP)
- A related process, called pulforming, is used to make parts that are curved and which may have variations in cross section throughout their lengths

Pultrusion

Continuous fiber rovings are dipped into a resin bath and pulled through a shaping die where the impregnated resin cures

- The sections produced are reinforced throughout their length by continuous fibers
- Like extrusion, the pieces have a constant cross section, whose profile is determined by the shape of the die orifice
- The cured product is cut into long straight sections
Materials and Products in Pultrusion

- Common resins: unsaturated polyesters, epoxies, and silicones, all thermosetting polymers
- Reinforcing phase: E-glass is most widely used, in proportions from 30% to 70%
- Products: solid rods, tubing, long flat sheets, structural sections (such as channels, angled and flanged beams), tool handles for high voltage work, and third rail covers for subways.
Pulforming

Pultrusion with additional steps to form the length into a semicircular contour and alter the cross section at one or more locations along the length

- Pultrusion is limited to straight sections of constant cross section
- Pulforming is designed to satisfy the need for long parts with continuous fiber reinforcement that are curved rather than straight and whose cross sections may vary throughout length


Pulforming Process

Other PMC Shaping Processes

- Centrifugal casting
- Tube rolling
- Continuous laminating
- Cutting of FRPs

In addition, many traditional thermoplastic shaping processes (e.g., blow molding, thermoforming, and extrusion) are applicable to FRPs with short fibers based on TP polymers.
Cutting Methods for Uncured FRPs

- Cutting of FRP laminated composites is required in both uncured and cured states
- Uncured materials (prepregs, preforms, SMCs, and other starting forms) must be cut to size for lay-up, molding, etc.
  - Typical cutting tools: knives, scissors, power shears, and steel-rule blanking dies
  - Nontraditional methods are also used, such as laser beam cutting and water jet cutting

Cutting Methods for Cured FRPs

- Cured FRPs are tough, abrasive, and difficult-to-cut
- Cutting of FRPs is required to trim excess material, cut holes and outlines, and so on
- For glass FRPs, cemented carbide cutting tools and high speed steel saw blades can be used
- For some advanced composites (e.g., boron-epoxy), diamond cutting tools cut best
- Water jet cutting is also used, to reduce dust and noise problems with conventional sawing methods