Environmentally Sustainable Polymer Development Through Feedstock Selection

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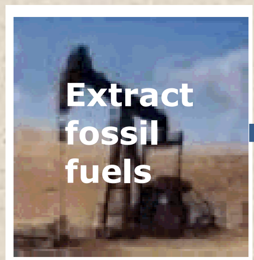
Scope

- Our focus today is on environmentally sustainable polymer development through feedstock selection
  - Approaches to environmental sustainability not based on feedstock selection, such as biodegradable polymer development, are outside the scope of this presentation

Outline

- Life cycle considerations for polymeric products
  - Thermoplastics
  - Thermosets
  - Elastomers/rubbers
  - Polymer matrix composites
- Use of biobased feedstocks as alternatives to fossil fuel based feedstocks
- Recycling of post-consumer products and scraps from product manufacturing
- Summary and conclusions

Typical Life Cycle of Virgin Polymeric Products Prepared from Fossil Fuel Based Feedstocks



→ Derive monomers → Manufacture polymeric products → Use polymeric products → Discard into landfill

Life Cycle Analysis (LCA)

- Crucial to assess environmental impacts of a new product comprehensively via LCA which considers these impacts through all stages of its life
  - Raw materials
  - Manufacture
  - Use
  - Maintenance
  - Final disposal
- See http://www.epa.gov/nrmrl/std/lca/lca.html for link to the document "*Life Cycle Assessment: Principles and Practice*" from which the diagram pasted onto the next slide was copied

Sample Life Cycle Stages for a Treatment Project

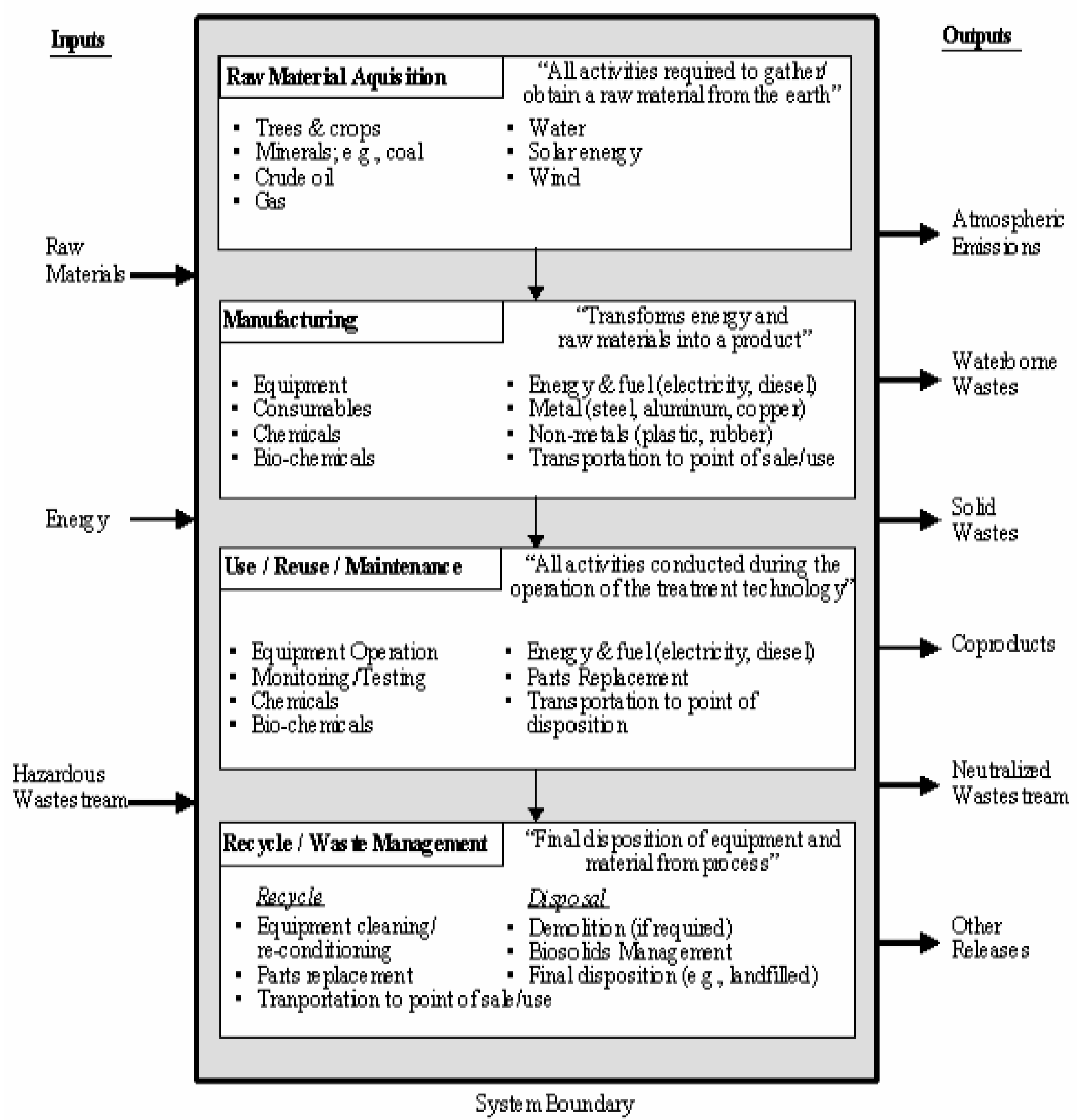


Exhibit 2-1. Sample Life Cycle Stages for a Treatment Project

Biobased Feedstocks: Market Considerations (1)

- Global plastics industry:
  - ~ $ 830 billion annual revenues
  - ~ 2.8% annual growth rate
- Biobased industry:
  - ~ $ 2.6 billion annual revenues
  - ~ 15% annual growth rate
- Many plants and microorganisms are biobased feedstock sources for obtaining and/or deriving monomers, oligomers, polymers, and/or biofibers

Biobased Feedstocks: Market Considerations (2)

- Substitution of biofeedstocks for petrochemical feedstocks often limited to partial replacement
  - Limitation due to need to avoid performance declines and/or price increases unacceptable to consumers who demand greater sustainability without making a sacrifice
- Price parity of biobased polymeric products with fossil fuel based counterparts is essential
  - Achievement of such parity by more biobased products will also depend on future abundance and prices of fossil fuels
  - For example:
    - Will fossil fuel extraction from unconventional resources become so widespread as to lead to a petrochemical industry renaissance?
    - Alternatively, will environmental concerns and/or faster renewable energy technology growth lead to a decline in fossil fuel extraction?

Biobased Content Determination

- ASTM D6866-12, "*Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis*" (11 May 2012)
- Used to measure biobased content of products containing carbon-based components combustible in presence of O_2 to produce CO_2 gas

$$\begin{array}{c}\text{\% BIO or BIOBASED CONTENT} \\ \text{\% Renewable Content}\end{array} = \frac{\text{BIO (Organic) CARBON}}{\text{TOTAL (Organic) CARBON}} * 100$$

- See "*Understanding Biobased Carbon Content*", Society of the Plastics Industry, Bioplastics Council (February 2012)

Some Significant Agricultural Sources of Biobased Feedstocks

- Starch: Corn, sugar cane, sugar beets
- Glucose: Corn, sugar cane, sugar beets
- Cellulose: Switch grass, bamboo, eucalyptus
- Vegetable Oil: Corn, soy, castor, rapeseed (canola), cottonseed, palm, algae
- Vegetable Protein: Soy
- Cellulosic Biofibers: Cotton, jute, kenaf, hemp, flax, sisal, ramie, corn, wheat, rice, sorghum, barley, sugarcane, pineapple, banana, coconut

Examples of Biobased Polymers

- From R. P. Babu, K. O'Connor, and R. Seeram, "*Current Progress on Bio-based Polymers and Their Future Trends*":

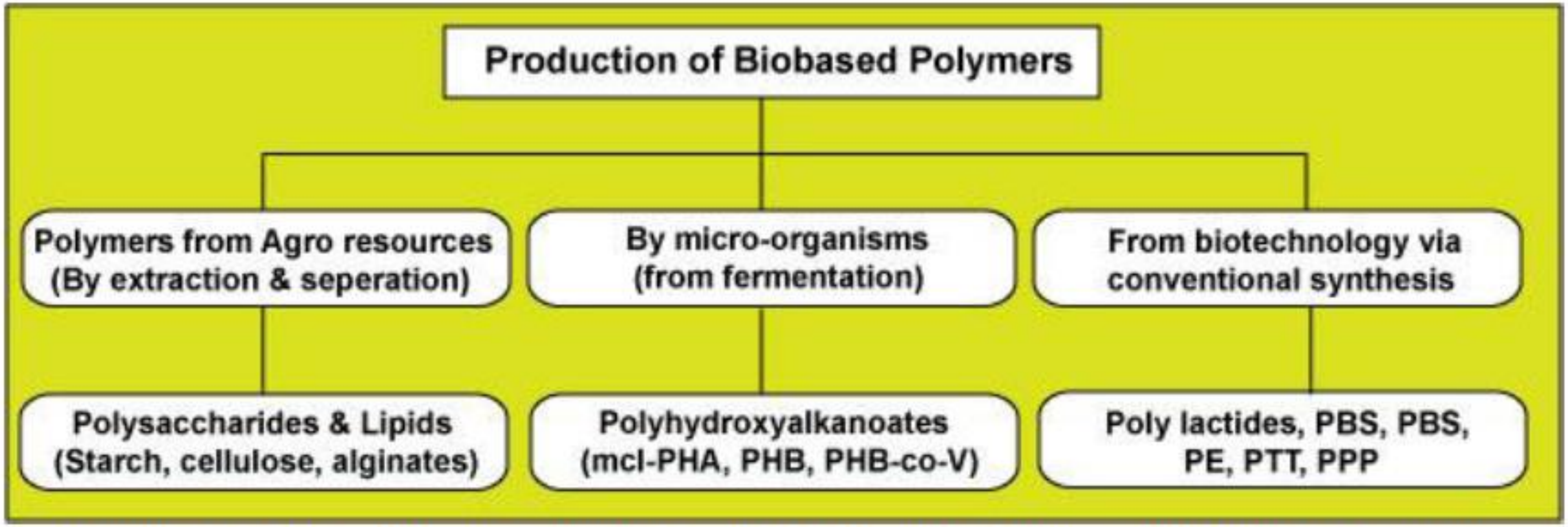
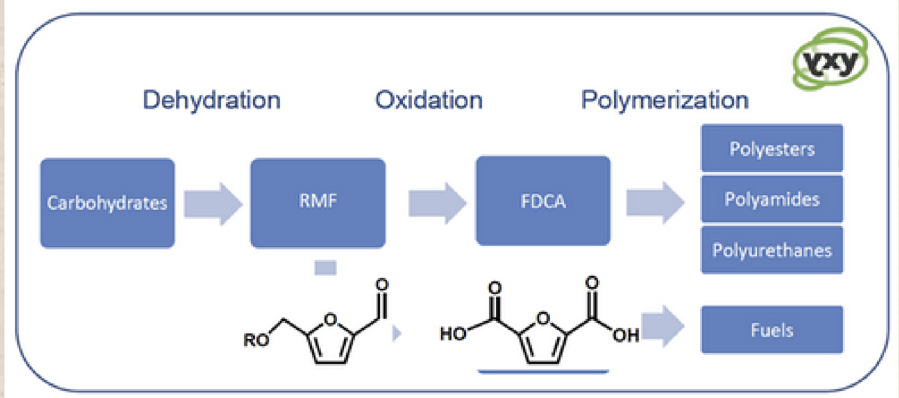
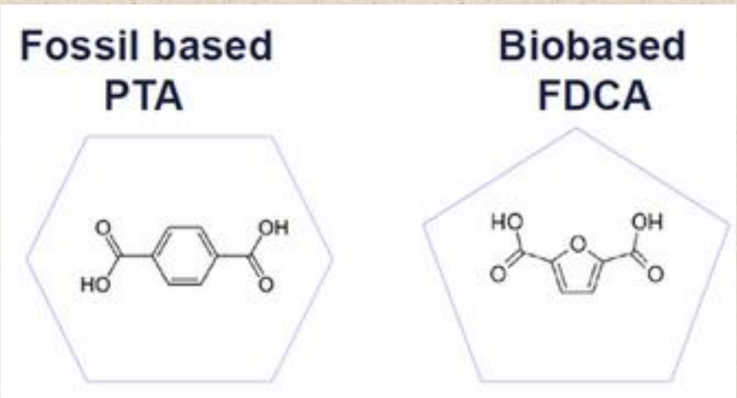
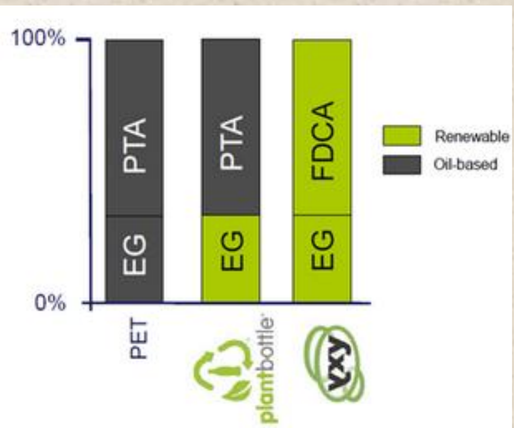


Figure 2: Most Common Categories of Bio-based Polymers Produced by Various Processes

More Examples: Furandicarboxylic Acid (FDCA) Polymers (Avantium)



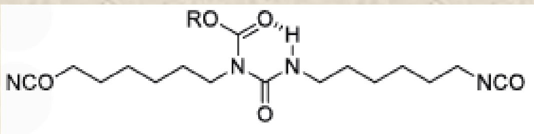


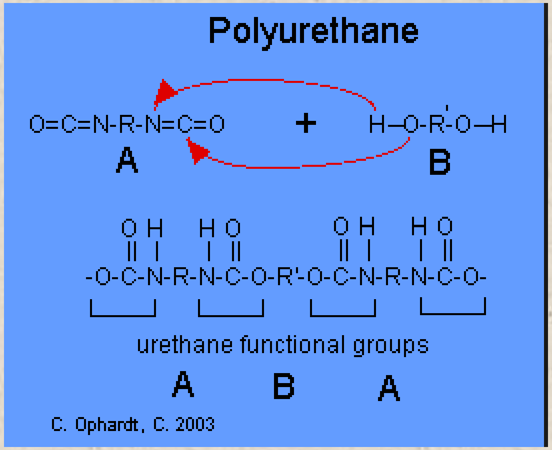


- Poly(ethylene furanoate) (PEF), prepared from FDCA and biobased ethylene glycol, is 100% biobased
- Properties of PEF comparable with those of poly(ethylene terephthalate) (PET) prepared from fossil fuel based terephthalic acid and ethylene glycol

More Examples: Polyurethanes Incorporating Biobased Ingredients

- Formed by reacting polyols with isocyanates
- Commercially available biobased polyols:
  - Agrol™ natural oil-based polyols (BioBased Technologies)
  - BiOH™ soy-based polyols (Cargill)
  - RENUVA™ natural oil-based polyols (Dow Chemical)
  - Bio-succinic acid-based linear (functionality=2) and branched (functionality=2.4 or 2.7) polyester polyols (Myriant)
  - Priplast™ biobased polyester polyols (Croda)
  - Cerenol™ polyether diols made with renewably sourced corn-based 1,3-propanediol (DuPont)
  - Biobased polyols (Vandeputte Oleo)
  - Sovermol™ biobased polyols (BASF)
  - EMEROX™ biobased polyols (Emery Oleochemicals)
- Only one commercially available partially biobased isocyanate:
  - Tolonate™ X FLO 100 partially biobased solvent-free low-viscosity aliphatic isocyanate (1,6-hexamethylene diisocyanate) polymer (Vencorex)





Challenges to Success: Land Resource Allocation Issues

- Use of agricultural feedstocks raises many issues whose severity can vary greatly between different crops as well as different geographical regions
  - Competition of land allocation for plant-based feedstock generation versus other purposes (i.e., food production)
  - Use of water for irrigation
  - Environmental impact of pesticide use
  - Environmental impact of fertilizer use
  - Level of penetration of genetically modified seeds
  - Natural habitat (such as Amazon rainforest) conversion

Challenges to Success: Technical Limitations

- Substitution of biofeedstocks for petrochemical feedstocks is often limited to partial replacement (as in polyurethanes) or not (yet?) possible at all
  - Many useful polymer formulation ingredients derivable from fossil fuel based feedstocks are not (yet?) available from biobased feedstocks
  - Ingredients available from biobased feedstocks often require expensive processes to derive and purify
- Many consumers demand greater sustainability but are unwilling to sacrifice performance or price
  - Frequent technical difficulty of providing a product with a similar performance at no higher a cost is a limitation

Polymer Recycling: Market Considerations

- Some recent facts about plastic waste recycling in the USA, from http://www.epa.gov/osw/conserve/materials/plastics.htm

  - 32 million tons of plastic waste were generated in 2012, representing 12.7 percent of total MSW.
  - In 2012, the United States generated almost 14 million tons of plastics as containers and packaging, about 11 million tons as durable goods such as appliances, and almost 7 million tons as nondurable goods, such as plates and cups.
  - Only 9 percent of the total plastic waste generated in 2012 was recovered for recycling.
  - In 2012, the category of plastics which includes bags, sacks, and wraps was recycled at about 12 percent.
  - Plastics also are found in automobiles, but recycling of these materials is counted separately from the MSW recycling rate.

- Polymer recycling rates vary significantly among countries but they could become much higher than they are today throughout the world
- Obviously there is a great opportunity here for industry to profit, while also contributing to environmental sustainability, by helping polymer recycling become more widespread and more cost-effective worldwide

Post-Consumer and/or Factory Scrap Polymer Recycling: Types of Technologies

- Mechanical recycling
- Chemical recycling
- Combined mechanical/chemical recycling
- Thermolysis

Mechanical Recycling Summary (1)

- Recovery of thermoplastic polymers from waste streams while preserving molecular structure, by:
  - Sorting waste stream into different recyclable polymers
    - Unless it was pre-sorted during collection
  - Shredding
  - Cleaning
    - Washing (most common)
    - Dry cleaning (with some advanced technologies)
  - Melt processing
    - Most commonly via extrusion
  - Filtration
    - Often while melt processing
  - Pelletizing

Mechanical Recycling Summary (2)

- Use-recycling-reuse cycles often lead to decline in quality, resulting in “downcycling”
  - Caused by one or a combination of:
    - Reduction of average molecular weight of polymer chains
    - Other chemical reactions causing undesirable changes in polymer
    - Accumulation of impurities
  - Limiting:
    - Reuse to products of increasingly lower value in successive cycles
    - Total possible number of cycles of use-recycling-reuse
- Equipment implementing processes differing in their details is sold by many manufacturers

Mechanical Recycling Example

- MAS Double Rotor Disk technology combined with MAS Extruder and Continuous Melt Filtration can be used to to recycle dirty plastic film and fibers
- No washing needed, so MAS claims as benefits:
  - No water use
  - No water usage permits
  - No waste water treatment
  - Less cost per pound
- http://www.youtube.com/watch?v=kCz8ZP4wdbo shows the system in operation for the shredding, dry cleaning, and pelletizing of agricultural film

Chemical Recycling Summary (1)

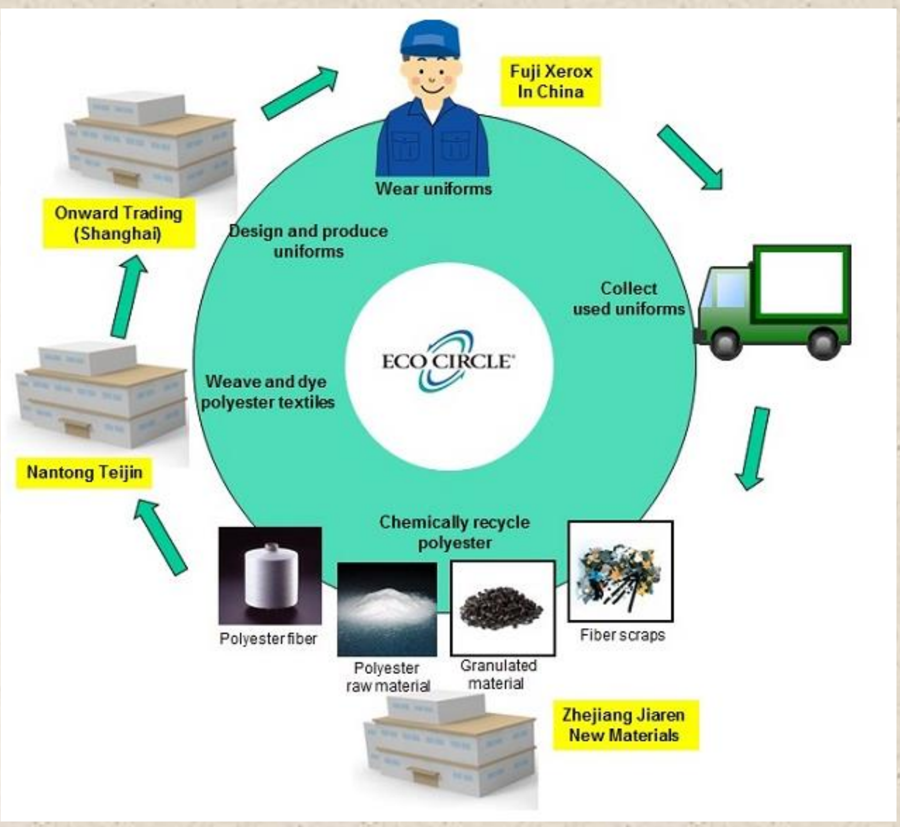
- Polymer depolymerized into its constituents
  - To oligomers in some implementations
  - All the way to monomers in some other implementations
  - Extent controllable by selection of process conditions
- Recovered and purified constituents can be used in manufacturing new products comparable in quality to those obtained from virgin monomers

Chemical Recycling Summary (2)

- Quality retained in repeated use-recycling-reuse cycles
  - Places target of “closed loop” recycling within reach
- “Upcycling” possible in some cases
  - Modify recovered constituents during depolymerization into constituents usable in polymers of higher value
  - I.e., partial depolymerization of PET combined with auxiliary reactions to obtain valuable aromatic polyols for use in polyurethane manufacturing
- But usually chemical recycling is more expensive than mechanical recycling!

Chemical Recycling Example

- 19th December 2013:
  "Teijin, Onward Holdings and Fuji Xerox will launch a closed-loop recycling system for uniforms in China. The system is based on Teijin's Eco Circle closed-loop recycling system that incorporates the world's first technology for the chemical recycling of polyester, according to the company."



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Combined Mechanical/Chemical Recycling

- Combine chemical reactions (depolymerization, chain extension, functional group attachment, etc.) with a mechanical recycling process
- Such reactive processing usually achieved by using reactive (instead of simple) extrusion

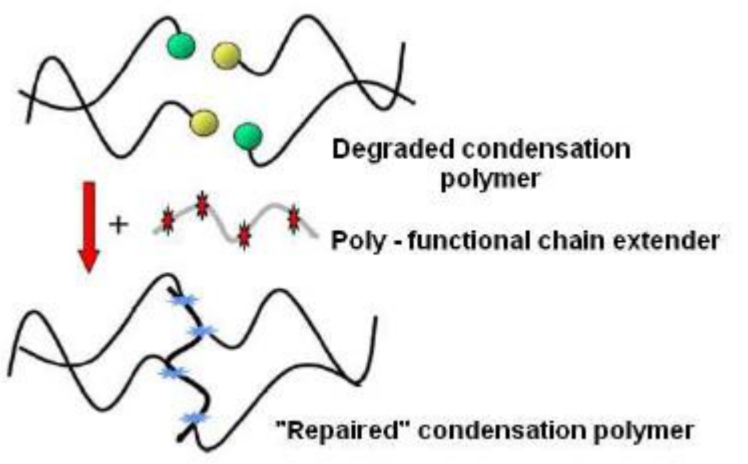

Fig. 6. Schematically presentation of the chain extension reaction (Villalobos et al., 2006).

Thermolysis Summary (1)

- Thermochemical decomposition into fuels whose energy content can be recovered is sometimes the most economically attractive option
- Often true for "hydrocarbon polymers" consisting of C and H with little or no heteroatom content
  - I.e., polyolefins, polystyrene, and some rubbers
- Also true for some very mixed waste streams but
  - Economics unfavorable if components with recoverable energy content are present at very low percentages

Thermolysis Summary (2)

- Depending on polymer molecular structure and process, various oils and/or gases are obtained
- Some rubbers contain large weight fractions of carbon black, a valuable formulation ingredient, which can also be recovered during thermolysis

Types of Thermolysis Processes

- Pyrolysis (thermal cracking in inert atmosphere)
- Hydrogenation (hydrocracking; namely, cracking by H_2 addition via chemical reaction)
- Gasification [thermooxidative cracking in air (cheaper and simpler process) or in O_2 (more expensive but more effective process)]

Thermolysis Example

- Agilyx converts previously non-recyclable and low value waste plastics into crude oil through an environmentally beneficial patented system
- The Agilyx Generation 6 System features the first continuous feed self-cleaning waste plastic processing system in the industry
- http://www.youtube.com/watch?v=-pngeJvLv20 summarizes the Agilyx technology

Challenges to Success: Waste Stream Supply Considerations (1)

- Recycling economics more favorable with:
  - Increasing quantity and steadiness of waste stream collected in geographical area
  - Social consciousness of residents
  - Infrastructure enabling residents to follow best practices
    - Simple pre-sorting (i.e., recyclable versus non-recyclable)
    - Placing different classes of recyclables into different collection containers
    - Washing some classes of recyclables before disposal

Challenges to Success: Waste Stream Supply Considerations (2)

- For example, here is Dr. Steve Chor Kie Wong's comparison of typical practices in Japan (left) and China (right):

Challenges to Success: Technology Improvements Needed

- Improved automated sortation of mixed waste streams
  - Methods such as flotation rely on density differences
  - Methods such as visible and near-infrared spectroscopy rely on optical properties
- Continued improvements of mechanical and combined mechanical/chemical recycling technologies to obtain product of higher quality so that “downcycling” is slowed and more cycles of use-recycling-reuse become possible
- Chemical recycling processes and thermolysis processes often need to become more cost-effective to be viable
- But, regardless of any technology improvements, waste stream supply considerations will still remain crucial in determining whether the economics become favorable!

Summary and Conclusions

- Life Cycle Analysis (LCA) is a guide to decision-making by assessing the environmental impacts of a new product comprehensively and quantitatively
- Two major approaches for environmentally sustainable polymer development through feedstock selection
  - Use of biobased feedstocks as alternatives to fossil fuel based feedstocks
  - Recycling of post-consumer products and scraps from product manufacturing
- State of the art reviewed for these approaches
  - Current technologies as well as challenges identified
  - In conclusion, both approaches present great opportunities for growing economic profits while simultaneously contributing to environmental sustainability