Sustainable Plastics: Evaluating the Chemistry of Plastics

BizNGO Meeting

December 1, 2011

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Purpose of Today's Talk

- Discuss background and need for evaluating plastics for both safety and sustainability
- Provide an overview and examples of assessment methods
- Identify training opportunities and information sources

BizNGO's Five Principles for Sustainable Plastics

- **BizNGO's Principles for Sustainable Plastics**
  - Sustainable Resources
  - Closed Loop Systems
  - Energy Efficient and Renewable
  - **Safer Chemicals**
  - **Healthy Workplaces and Communities**

- **Safer Chemicals**
  - A plastic should be manufactured using inherently safer chemicals and processes. The byproducts and waste streams from manufacturing along with the degradation and transformation products from use and end-of-life management should be inherently safer and in balance with natural systems.

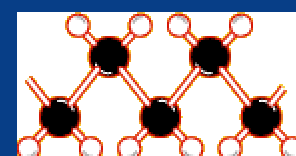
- **Healthy Workplaces and Communities**
  - Industry practices at each stage in the life cycle of a plastic, from the growing or extracting of feedstocks to the manufacturing of a plastic and its end-of-life management should be healthy for workers, local communities and the environment.

Plastics: Past and Future

What are Plastics?

- The Greek word *plasticós* means "to mold”
- Plastics consist of polymers (i.e., long molecule chains) often formulated with other ingredients (stabilizers, plasticizers, fillers, colorants, etc.)
  - Common sources for conventional plastics are carbon compounds sourced from oil (petroleum) and natural gas
- Plastics are polymers, but polymers don't have to be plastics
  - Ex.: Cellulose, the basic component of plant cell walls is a polymer, as is DNA, silk, wool, and leather

Ethylene monomer



Polyethylene

PE Resin

Plastic Building Blocks

Plastics: Past and Future

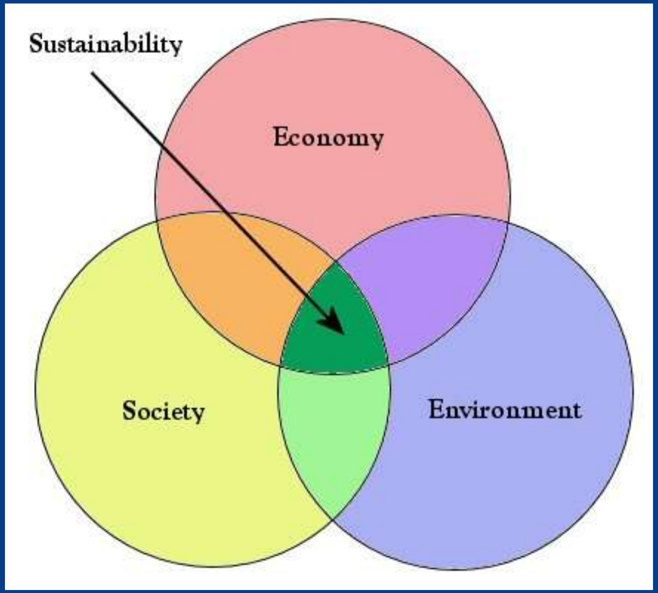
- Plastics are classified into two categories based on what happens when they're heated:
  1) Thermoset: any material that, once heated, cannot be reheated or reformed (e.g.,: Bakelite, Melamine, Teflon, Torlon, Celazole, glass epoxy systems, phenolic)
  2) Thermoplastic: any material that can be heated and reheated to make a finished part or stock shape (e.g.,: PVC, PE, nylon, acetal, acrylic)

- 80% of plastics produced are thermoplastics
  - PE, PP, PS, and PVC are the most commonly used (approx. 70%)

- Properties of a plastic depend on the polymer chains, how chains are bonded to each other, and what additives are present
  - These properties affect the intrinsic hazard of the plastic and its life cycle

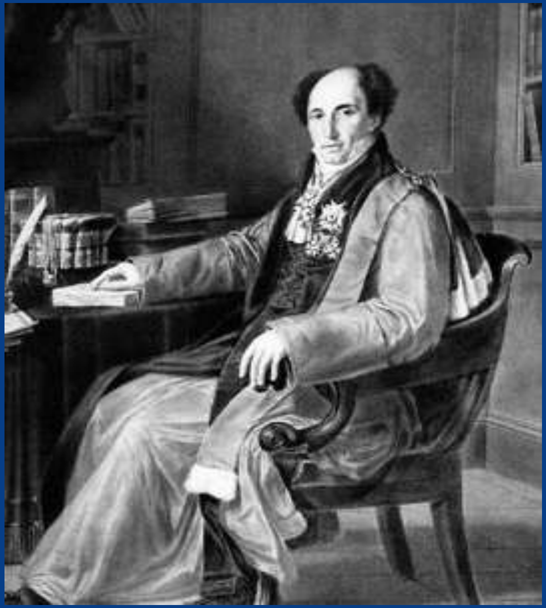
Sustainable Plastics & Toxicology

- Historically, toxicologists have protected the safety of <u>humans</u>
  - Environmental issues took a back seat to human health
  - However, over the past 20 years, this focus has expanded to consider effects on ecosystems and non-human organisms
    - Toxicologists must consider both human health and environmental health



Toxicology: Balancing Safety and Sustainability

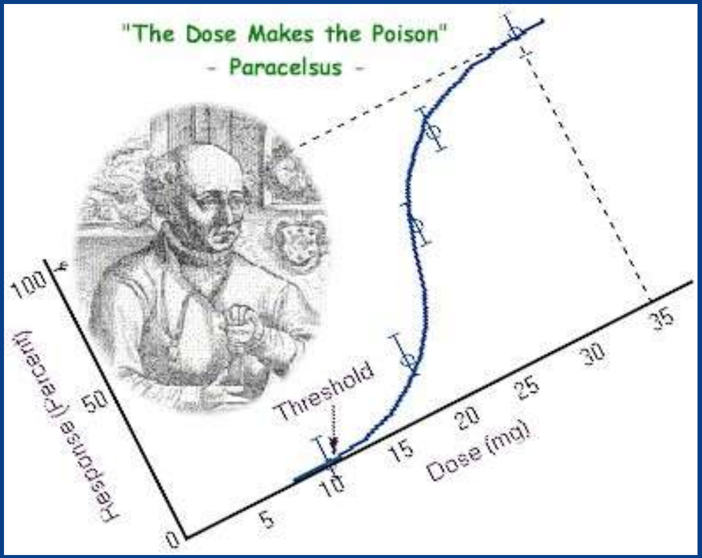
- The protection of human health alone is no longer the sole aim of toxicology
- Consider SOT's definition of toxicology:
  - Toxicology is the study of the adverse effects of chemical, physical or biological agents on living organisms and the ecosystem, including the prevention and amelioration of such adverse effects.



Orfila

Protecting Humans and the Environment

- Key Concepts for Human Health Protection Are Still Valid Under this Expanded Paradigm of Hazard Prevention
  - In sufficient quantities, *everything* has the potential to be toxic to humans
  - Salient questions: What factors influence toxicity?
    - The dose (primary factor)
    - Chemical structure
      - Influences toxicokinetics (A,D,M,E)
      - Influences toxicodynamics (i.e., mechanism by which a toxic effect is produced in the cell)
    - Route of exposure
    - Host factors
      - Very young and very old more susceptible



Safety: Environmental Protection

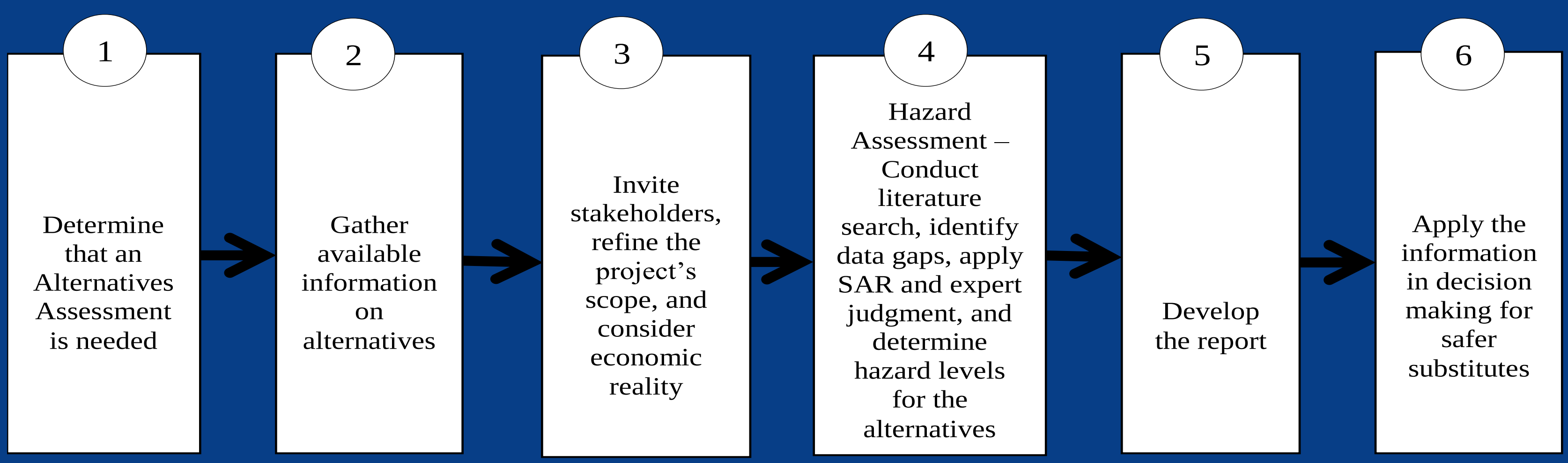
- Key Concepts for Environmental Protection
  - Chemicals may pose hazards to aquatic, terrestrial organisms, and/or plants
  - Four specific properties predict whether a chemical poses an environmental hazard
    - **Aquatic or terrestrial toxicity**: The hazard of a substance to living organisms, based on toxicity tests to aquatic or terrestrial animals and plants
    - **Degradability**: The persistence of the substance in the environment, based on molecular structure or analytical testing
    - **Bioaccumulation/bioconcentration**: The accumulation of a substance in living organisms (from water sources for bioconcentration), which may or may not lead to a toxic effect

Challenges to Performing Plastics CAA

- The paradigm for CAA is well established for non-polymeric ingredients of plastics
- Assessing hazards of polymers is more challenging:
  - Incomplete datasets for health/environmental endpoints for most polymers
  - Very difficult to perform “read across” on polymer surrogates
    - Limited publically accessible toxicity data on surrogates
    - Differences in polymer characteristics limit read-across to other datasets
    - The absence of data does **not** equate with the absence of hazard!!

Promoting Safety and Sustainability: Chemicals Alternatives Assessments (CAA)

- CAA is the primary tool to evaluate and manage hazards through the informed choice of safer chemicals
  - CAAs are designed to evaluate and manage hazards through the informed choice of safer chemicals
  - EPA's DfE Program developed a six step CAA paradigm:



Six Broad Steps in Conducting a DfE Alternatives Assessment (From Lavoie et al. 2010)

Chemicals Alternatives Assessments (CAA)

- Two primary CAA paradigms are in use
  - U.S. EPA’s Design for the Environment (DfE) Alternatives Assessment Criteria

  http://www.epa.gov/dfe/alternative_assessments.html
  - BizNGO’s CAA Paradigm (which incorporates) Clean Production Action’s Green Screen (updated Oct, 2011)
  - *www.bizngo.org/CAAProtocol and*

  http://www.cleanproduction.org/Greenscreen.php

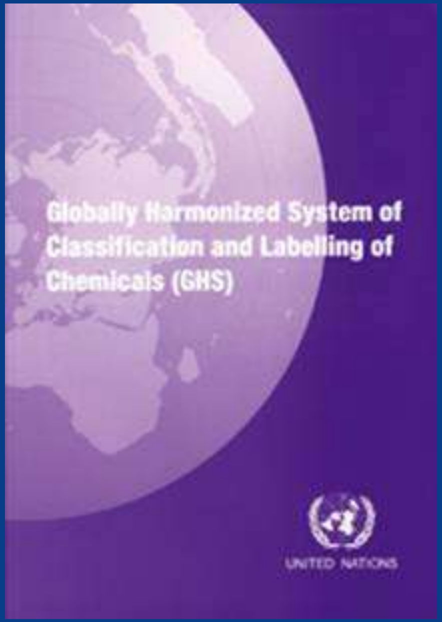
- Both paradigms assess a broad range of health effect and environmental endpoints
  - As an example, DfE’s CAA estimates hazards for 21 individual health effect endpoints and 14 environmental endpoints
  - See Lavoie et al. (2010): http://pubs.acs.org/doi/abs/10.1021/es1015789

Chemicals Alternatives Assessments (CAA)

- A CAA is based on primary data, data on chemical surrogates, and predictive modeling
- A CAA comprises a literature search, identification of critical effects and data gaps, chemical analog selection and QSAR modeling, all applied to a broad set of toxicological and environmental endpoints
- The overall **goal** is to ascertain whether a proposed chemical alternative is less hazardous to human health and the environment

Performing CAAs: Three Steps

- Step One: Read CAA criteria
  - Links to DfE and Green Screen provided previously
- Step Two: Understand hazard classification according to GHS
  - GHS is a system for standardizing and harmonizing the classification and labeling of chemicals.
  - GHS defines health, physical and environmental hazards of chemicals
  - See http://www.osha.gov/dsg/hazcom/ghs.html
  - Numerous organizations have training sessions: for example: http://www.chemadvisor.com/Training.aspx



- Step Three: Become proficient in assessing toxicology and environmental studies, as well as using and interpreting output from analog and QSAR software (see slide at end)

Challenges to Performing Plastics CAA

Plastic CAA

- A plastic contains 10-30 chemicals
  - Each ingredient is assessed as part of the overall hazard evaluation of the plastic material
  - Green Screen v 1.2
    - Performing CAA on a plastic comprises individual assessments for each intentionally added ingredient and chemicals present at $\geq$100 ppm (0.01%)
      - 1000 ppm (0.1%) may be used as threshold if lower one is not feasible

http://www.cleanproduction.org/library/greenScreenv1-2/DRAFT_GreenScreen_v1-2_Guidance_2011_1018_v2.pdf

CAA: Stearic Acid Example

D = Endpoint characterized by existing data MD = Modeled data used ND = No data or inadequate data
VL = Very Low L = Low M = Moderate H = High VH = Very High

Existing Data Summary Table – Human Health Endpoints

Acute Toxicity: Low	
Acute oral	D (L)
Acute dermal	D (L)
Acute inhalation	ND
Irritation and Corrosion: Moderate	
Eye irritation	D (M)
Dermal irritation	D (L)
Sensitization: Low	
Skin sensitization	D (L)
Respiratory sensitization	ND
Repeated Dose Toxicity: Low	
Repeated dose oral	D (L)
Repeated dose dermal	D (L)
Repeated dose inhalation	ND
Reproductive and Developmental Toxicity: Low	
Reproductive toxicity	D (L)
Developmental toxicity	ND

Carcinogenicity: Low	
Carcinogenicity (human)	ND
Carcinogenicity (animal)	D (L)
Mutagenicity/Genotoxicity: Low	
Gene mutation *in vitro*	D (L)
Gene mutation *in vivo*	ND
Chromosomal aberrations *in vitro*	ND
Chromosomal aberrations *in vivo*	N/D
DNA damage and repair	D (L)
Neurotoxicity: No Data	
Neurotoxicity	ND
Endocrine Activity: No Data	
Endocrine activity	ND

Existing Data Summary Table – Ecotoxicity and Environmental Fate

Ecotoxicity	
Acute Aquatic Toxicity: Moderate	
Acute fish LC_{50}	D (M)
Acute daphnia LC_{50}	D (H)
Acute mysid shrimp LC_{50}	ND
Acute green algae EC_{50}	D (M)
Chronic Aquatic Toxicity: Very High	
Chronic fish LOAEC	MD (VH)
Chronic daphnia LOAEC	MD (VH)
Chronic mysid shrimp LOAEC	ND
Chronic green algae LOAEC	MD (VH)

Environmental Fate	
Persistence: Very Low	
Water	D (VL)
Soil	D (VL)
Sediment	D (VL)
Air	n/a
Bioaccumulation: High	
Bioaccumulation factor	MD (H)
Bioconcentration factor	MD (L)

A DfE CAA will evaluate 21 individual health effect endpoints and 14 environmental endpoints

- **Data can be on the chemical itself, a chemical surrogate, or a modeled value**
- **Each CAA takes from 25-30 hours of time**
- **A CAA on a plastic ingredient such as stearic acid is relatively easy to perform due to robust dataset**

CAA: Health Effects of Stearic Acid

Human Health Hazard Summary- Rubber Formulation																						
Human Health Endpoints																						
		Acute Toxicity			Irritation and Corrosion		Sensitization		Repeated Dose Toxicity			Reproduct. and Develop. Toxicity		Cancer		Mutagenicity/Genotoxicity					Neuro.	Endocrine Activity
Chemical	CAS#	Acute Oral	Acute Dermal	Acute Inhalation	Eye Irritation	Dermal Irritation	Skin Sensitization	Respiratory	Repeated Dose Oral	Repeated Dose Dermal	Repeated Dose Inhalation	Reproductive Toxicity	Developmental Toxicity	Carcinogenicity (Human)	Carcinogenicity (Animal)	Gene Mutation *in vitro*	Gene Mutation *in vivo*	Chromo Aberrations *in vitro*	Chromo Aberrations *in vivo*	DNA Damage and	Neurotoxicity	Endocrine Activity
Stearic acid	57-11-4	D (L)	D (L)	ND	D (M)	D (L)	D (L)	ND	D (L)	D (L)	ND	D (L)	ND	ND	D (L)	D (L)	ND	ND	ND	D (L)	ND	ND
Dicyclohexyl-amine	101-83-7	D (H)	D (H)	ND	D (H)	D (VH)	ND	ND	ND	ND	ND	ND	ND	ND	ND	D (L)	ND	ND	ND	ND	ND	ND

[1] D = Endpoint characterized by existing data MD = Modeled or analog data used ND = No data or inadequate data
VL = Very Low L = Low M = Moderate H = High VH = Very High

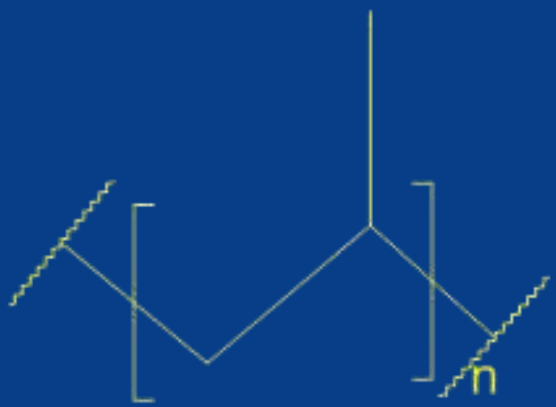
CAA: Environmental Effects of Stearic Acid

Ecotoxicity and Fate Hazard Summary- Rubber Formulation															
Ecotoxicity and Environmental Fate															
		Acute Aquatic Toxicity				Chronic Aquatic Toxicity				Persistence				Bioaccumulation	
Chemical	CAS#	Acute Fish LC50	Acute Daphnia LC50	Acute Mysid Shrimp L50-	Acute Green Algae EC50	Chronic Fish LOAEC	Chronic Daphnia LOAEC	Chronic Mysid Shrimp LOAEC	Chronic Green Algae LOAEC	Water	Soil	Sediment	Air	Bioaccumulation Factor	Bioconcentration Factor
Stearic acid	57-11-4	D (M)	D (H)	ND	D (M)	MD (VH)	MD (VH)	ND	MD (VH)	D (VL)	D (VL)	D (VL)	n/a	MD (H)	MD (L)
Dicyclohexylamine	101-83-7	D (H)	MD (VH)	MD (VH)	D (VH)	MD (VH)	MD (VH)	MD (VH)	MD (VH)	MD (L)	MD (M)	MD (VH)	n/a	ND	MD (H)

[1] D = Endpoint characterized by existing data MD = Modeled or analog data used ND = No data or inadequate data
VL = Very Low L = Low M = Moderate H = High VH = Very High
[2] For this endpoint, High/Moderate/Low etc. characterizations will not apply. A qualitative assessment of available data will be prepared.

Polymer CAA

- **Polypropylene (CAS #9003-07-0)**



% of Each Monomer
- Monomer 1
- Monomer 2
- Monomer 3

Are the monomers blocked? (Y/N)

Molecular Weight (MW) of Polymer

% of Polymer with
- MW <500
- MW <1,000

% Weight Residual Monomers

Solubility/Dispersability/Swellability

Particle Size

Overall Polymer Charge

Identify constituents and residual concentrations of
- Catalysts
- Processing aids

Many recently developed polymers are not completely characterized in terms of their polymeric composition

Polymer CAA

- EPA's Sustainable Futures Initiative developed guidelines for assessing polymers: http://www.epa.gov/oppt/sf/pubs/iad_polymers_042010.pdf
- EPA's polymer assessment guidelines provide assessment methods for estimating:
  - Physical/chemical properties of polymers
  - Environmental fate of polymers
  - Aquatic toxicity of polymers
  - Human health hazard of polymers

Polymer CAA

- Challenges posed by polymers
  - Lack of data/incomplete datasets
  - Proprietary nature of polymers limits data sharing

Green Screen Hazard Ratings																				
Group I Human					Group II and II* Human									Ecotox		Fate		Physical		
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F	
						single	repeated*	single	repeated*											
L	L	M	L	dg	L	dg	M	dg	dg	L	dg	L	dg	M	dg	H	L	L	L	

Functional Use	Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	On CPA Red List?	Green Screen Rating
Plastic and pesticide manufacturing	End of Life	Degradation	Piperazine	110-85-0	N	n/a
Chemical intermediate	End of Life	Degradation	Diphosphoric acid	2466-09-3	N	n/a
Multiple	End of Life	Degradation	Phosphoric acid	7664-38-2	N	n/a

Table 1: REDACTEDGreen Screen Summary

Chemical	CASRN	Human Health Effects									Aquatic Toxicity		Environ-mental		GS Benchmark Score
		Acute Toxicity	Skin Sensitizer	Cancer Hazard	Immunotoxicity	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	
Arnitel XG Material															
[REDACTED]															
[REDACTED]	[REDACTED]	*M*[a,b]	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	**V**[d]	*L*	**3**
[REDACTED]															
[REDACTED]	[REDACTED]	*M*[a,b]	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	**V**[d]	*L*	**3**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**[b]	**L**	*L*	*L*	**L**	**L**	*L*	**L**	**L**	**L**	**M**	**V**[d]	**L**	**2**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	**L**	**M**	*L*	**L**	**L**	*L*	**H**	**L**	*L*	**M**	**H**	**L**	**2**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	**L**	*L*	*L*	**L**	**L**	*L*	*L*	**L**	*L*	*L*	**H**	**L**	**2**
[REDACTED]	[REDACTED]	**L**	*L*	**L**	*L*	**L**	**L**	*L*	**L**	**L**	**L**	**L**	**L**	**L**	**4**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	**M**	**L**	*L*	**H**	**H**	*L*	**L**	**L**	**H**	**H**	**V**[d]	**H**	**1**
[REDACTED]	[REDACTED]	**L**	**M**	**L**	*L*	**H**	**H**	*L*	**L**	**L**	**H**	**H**	**V**[d]	**H**	**1**
[REDACTED]															
[REDACTED]	[REDACTED]	*M*[a,b]	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	**V**[d]	*L*	**2**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	**L**	*L*	*L*	**L**	**L**	**L**	**L**	**L**	**L**	**L**	**V**	**L**	**2**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	**L**	*L*	*L*	*L*	*L*	**M**	**L**	**L**	**L**	*L*	**H**	M	**2**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	**L**	*L*	**L**	**L**	*L*	*L*	**L**	**L**	**L**	**L**	**V**[d]	*L*	**2**
[REDACTED]															
[REDACTED]	[REDACTED]	**L**	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	**4**

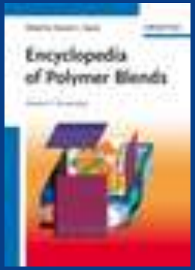
L=Low Hazard M[1]=Moderate Hazard H=High Hazard, V- Very High Hazard-Endpoints in colored text (L,M, and H) were assigned based on experimental data. Endpoints in black italics (*L*, *M*, or *H*) were assigned using estimated values and professional judgment (Structure Activity Relationships)

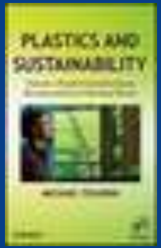
Upcoming Training:Tox- Related

- GHS Training
  - http://www.chemadvisor.com/Training.aspx
- EPA's Sustainable Futures Training
  - Instruction in software used to model physical/chemistry and health effect and ecological endpoints (e.g., EPiSuite, Oncologic, AIM, and Ecosar)
  - http://www.epa.gov/opptintr/sf/meetings/train.htm#how
- QSAR Modeling
  - OECD Toolbox Training will be held in Barcelona, Spain in mid-February, 2012 (2/13-2/15)
  - Will soon be open for registration at: http://www.qsari.org/index.php/training

Plastics: Training and Information

- Industry Webinars/Conferences
  - Smithers Rapra webinars (www.rapra.net)
    - Biopolymers (Dec 14, 2011)
    - Avoiding Failure of Plastic Products (Dec 15, 2011)
    - Plastics Recycling and Sustainability (Dec 13, 2011)
  - Green Polymer Chemistry (Cologne, Germany, March 20-22, 2012
    - http://www2.amiplastics.com/Events/Event.aspx?code=C412&sec=1853
  - Bioplastics (San Francisco, CA, June 13-15, 2-12)
    - http://www.bioplastix.com/program.htm
- Emails/Newsletters
  - SpecialChem's plastics updates: http://www.specialchem4polymers.com/
  - Plastics News Sustainability Report weekly newsletter: http://www.plasticsnewsglobalgroup.com/mailings/global_signup.html
- New Books from Wiley
  - http://www.wiley.com/WileyCDA/Section/id-612013.html
  - Sign up for auto-email on chemistry publications at: http://dmmsclick.wiley.com/optin.asp?sid=2YR5XS28WWNDWCKVHUKN&id=152





Conclusion

- Plastics can be formulated to be less hazardous and more sustainable following BizNGOs Principles of Sustainability, along with the application of CAA tools
- Continuous improvement in plastics can be spurred through expansion of databases such as CleanGredients so that greener commodity additives can be easily identified
- Further refinement of CAA methods is needed for polymeric ingredients used in plastics
- Accuracy of CAAs for polymeric ingredients can be improved by expanding datasets
  - Polymeric characterization (see SF guidance for endpoints)
  - Basic datasets on polymer (acute toxicity, acute aquatic toxicity, biodegradation)

Thank You!!

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