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APPROVAL DATE:
06/05/2007
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FTS-03: LDPE -MATERIAL SAFETY DATA SHEET

1. Product and company identification

Product identification	LDPE
Manufacturer	Rompetrol Petrochemicals S.R.L., company of Rompetrol Group DJ226, KM23, COD 905700, CONSTANTA, ROMANIA Tel: +(40) 241 506 868 Fax: +(40) 241 506 909

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2. Composition/information on ingredients

Chemical name: low density polyethylene
Synonyms: LDPE

Composition:	**CAS #**	**% m/m**
Low density polyethylene	9002-88-4	> 98
Additives	-	<2

Physical appearance: White powder, translucent to white pellets. Various organic and inorganic additives may be incorporated. If the product is used in food and pharmaceutics industry, a sanitary notice must indicate this.
Immediate concerns: Spilled material may present a slipping hazard. Following handling and packing various procedures, polyethylene dust may occur. When accumulate in the air, polymer dust may reach an explosion hazard concentration. Molten polymer may cause thermal burns. When burning without sufficient oxygen, it starts to release fumes that can contain carbon mono and dioxide, other oxidation organic compounds. To minimize exposures, adequate room and ventilation should be provided.

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3. Hazard identification

Polyethylene is not classified as toxic, harmful, irritant or corrosive product.

Eye contact: The product may contain small particles that may cause eyes irritation, due to the mechanical action. Gaseous emissions released while burning may cause eyes irritation/redness.
Skin contact: The product may contain small particles that may cause irritation. The contact with molten polymer causes thermal burns.
Ingestion: The product presents minimal toxicity. No hazard anticipated from swallowing incidental small amounts.
Inhalation: In normal concentrations, polymer dust induces no health effects. The product is not volatile at room temperature. Gaseous emissions released while burning may cause nose and breathing tract irritation.

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4. First aid measures

Eye contact: Flush with plenty of water for 15 minutes. Remove large particles. In case the irritation persists, get medical attention.
Skin contact: Flush with water and soap for several minutes. In case the irritation persists, get medical attention. Molten polymer – if molten material comes in contact with the skin, cool under ice water or a running stream of water, in any case not with ice. Cover the affected area with clean cotton sheet or gauze. Do not attempt to remove the material from skin; it could result severe tissue damage. Get medical attention.
Ingestion: Not applicable
Inhalation: In case typical symptoms occur, remove the victim to fresh air. Get medical attention if symptoms persist.

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5. Fire fighting measures

Flashpoint: > 340°C
Ignition conditions: Polyethylene is a combustible substance but under normal housekeeping conditions there is no risk of ignition. In contact with a flame it becomes soft, flows, ignites and burns with a light flame until exhausting (if it isn't stabilized with a flame retardant agent). Static electricity easy accumulates during handling/storage and may constitute an ignition source in case a high dust concentration exists.
Toxic combustion products: Carbon mono and dioxide, other oxidation organic compounds. In case of burning without sufficient oxygen, a black, dense smoke is released
Extinguishing media: Small fire: dry chemicals, and carbon dioxide extinguishers. Large fires: large quantities of water spray.
Fire fighting procedures: Keep people away. Isolate fire area and deny unnecessary access. Cool the area with water to localize the fire. Soak with water to cool and to avoid re-ignition.
Protective equipment for fire fighters: Complete fire fighting clothing, self-contained breathing apparatus. In case these are not available, fire extinguishing has to be done from a safe distance or a protected location. .
Explosion hazard: The product as delivered has no explosive character. In case of accumulation, polymer dust may form explosive mixtures with the air.

6. Accidental release measures

Personnel protection*:* Remove unnecessary personnel from area. Limit access to the area. Spilled pellets may induce slipping hazard. Molten polymer presents thermal burns hazard in case of skin contact.
Environment protection*:* The released material will not be discharged to the sewerage.
Clean up: The contaminated area shall be swept and cleaned, and the residual material collected in dried and labeled containers. For disposal, see section 13.

7. Handling and storage

Store polyethylene in dark, dry and well-ventilated area, away from all heat and ignition sources (sparks, open flames or hot surfaces, welding operations), combustible materials or incompatible substances (benzene, chlorophorm, decalin). Temperature in the storage area shall not exceed 40^0C. Avoid dust accumulation by frequent cleaning and suitable warehouses structure. Local exhaust ventilation is recommended for control of airborne dust, fumes and vapors, in enclosed areas.
During handling and processing, polymer may charge electrostatic. Use only machines fitted with earth.

8. Exposure control / personal protection

Eyes and hands protection: Safety glasses for handling at ambient temperature. Thermal resistant gloves, arm protection and goggles/face shield in case of possible contact with molten product.
Skin and body protection: In case of polymer handling or processing at elevated temperatures or in a molten state, adequate protective equipment will be used over the skin, to prevent contact.
Respiratory protection: For most conditions, no special respiratory protection is necessary. When polymer is heated, general and local ventilation systems will be provided.
Hygienic measures: Inside work areas, eating is not allowed. Normal clothing will be kept separately from work and protective equipment.

9. Physical and chemical properties
Physical state: Pellets, powder
Color: White translucent
Odor: No odor
Melting temperature: 130-160 °C
Flash point: > 340 °C
Density: 0.91 - 0.94 g/cm^3
Water solubility: Negligible

10. Stability and reactivity

Chemical stability: Polyethylene pellets are normally stable. The product is not corrosive.
Hazardous polymerization: No
Conditions to avoid: Excessive temperatures, sparks or open flames.
Materials to avoid: Solvent substances (benzene, chlorophorm, decalin).
Hazardous decomposition products: Carbon mono and dioxide, other oxidation organic products.

11. Toxicological information

Acute toxicity: Polyethylene is considered non-toxic for animals, in case of powder inhalation or solid swallowing.
Local effects: Unknown
Sensibility: Unknown
Chronic toxicity: Unknown
Cancer hazard: Not established
Maximum concentration accepted: Not regulated.
As a limitation, the dust level – according OSHA limits - must not exceed 15 mg/m^3 for total dust and 5 mg/m^3 for respirable dust. According ACGIH, the limit for total dust is 10 mg/m^3. If toxic impurities or decomposition products appear, it has to take into consideration the smallest limits stipulated in local or national legislation.

12. Ecological information

Movement: Soil- the product will not migrate. Water – the product will float.
Degradation: The product is inert and it is not biodegradable. Surface photo degradation is expected with exposure to sunlight. Due to the negligible water solubility, it produces no effects on aquatic environment.
Bioaccumulation: Not expected
Ecotoxicity: Minimal, due to the negligible water solubility. Pellets may be harmful for birds and fish if swallowed.

13. Disposal considerations

Spilled material removal: Sweep and clean contaminated area, collect residual material into dried, labeled containers. Wash the area with water.
Wastes disposal: Polyethylene is a recyclable material. It is preferably that production rejects and conversion wastes be recycled instead of being disposed.
Disposal of any wastes should respect all national and local valid regulations. If these regulations are met, the following is applicable for polyethylene, as supplied; additives, fillers or other materials addition involves their influence consideration, on the afferent documentation basis. Polyethylene can be disposed by landfill or controlled incineration, respecting valid regulations regarding gaseous or solid particles discharges. Due to the high heat value, incineration has to be done only in units designed to handle high heats of combustion. In case it is landfilled: polyethylene is inert, does not degrade quickly, form a strong and permanent soil base and does not release gases or other compounds known to pollute water resources.

14. Transport information

International settlements: not regulated by RID, ADR, DOT, IATA, ICAO, IMDG rules.

Polyethylene pellets transport: CP4 euro pallets (1375 kg LDPE/pallet, distributed in polyethylene bags, containing each one 25 kg of product), big-bags- in truck or rail silo, maritime transport containers
Polyethylene powder transport: polyethylene bags, containing each one 25 kg of product, big-bags- in truck or rail silo.

15. Regulatory information

According valid Romanian legislation:

Label:	**Hazard symbol:**	Not regulated
	R - phrases:	Not regulated
	S - phrases:	Not regulated

According international legislation: To the best of Rompetrol Petrochemicals knowledge, the product contains no chemical subject to SARA /Title III, OSHA or CERCLA requirements.

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16. Other information

Rompetrol Petrochemicals does not recommend any company product for applications that involve human tissues or internal fluids contacts (regardless of the contact length of time), for cardiac devices, for medical device components that support human life, as well as for applications that have connections with human reproduction.

The information relates only to the specific product described above and not to use of the product in combination with other materials. The information contained in this material has been compiled from sources that Rompetrol Petrochemicals considers reliable and accurate. However, the information is provided without any warranty, expressed or implied, regarding its correctness and completeness. Because use conditions and valid regulations may differ from one location to another and may change in time, the customer is responsible for deciding whether the product and the information in this document are suitable for his use and for ensuring that his workplace or disposal practices are in compliance with valid legal regulations. To determine applicability or effects of any law or regulation with respect to the product, user should consult his legal advisor or the appropriate government agency. Rompetrol Petrochemicals does not undertake to furnish advice on such matters. Rompetrol Petrochemicals does not assume nor authorize anyone to assume on Rompetrol Petrochemicals behalf any liability with the use of the information in this MSDS.
The conditions or methods of handling, storage, use and disposal of the product are beyond our control and may be beyond our knowledge. For this, we do not assume responsibility for loss, damage, or expense arising out or connected with handling, storage, use or disposal of this product.

FTS-03: LDPE -MATERIAL SAFETY DATA SHEET

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DJ226, KM23, COD 905700, CONSTANTA, ROMANIA
Tel: +(40) 241 506 868 Fax: +(40) 241 506 909

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Synonyms: LDPE

Composition:	**CAS #**	**% m/m**
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Additives	-	<2

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3. Hazard identification

Polyethylene is not classified as toxic, harmful, irritant or corrosive product.

Eye contact: The product may contain small particles that may cause eyes irritation, due to the mechanical action. Gaseous emissions released while burning may cause eyes irritation/redness.
Skin contact: The product may contain small particles that may cause irritation. The contact with molten polymer causes thermal burns.
Ingestion: The product presents minimal toxicity. No hazard anticipated from swallowing incidental small amounts.
Inhalation: In normal concentrations, polymer dust induces no health effects. The product is not volatile at room temperature. Gaseous emissions released while burning may cause nose and breathing tract irritation.

4. First aid measures

Eye contact: Flush with plenty of water for 15 minutes. Remove large particles. In case the irritation persists, get medical attention.
Skin contact: Flush with water and soap for several minutes. In case the irritation persists, get medical attention. Molten polymer – if molten material comes in contact with the skin, cool under ice water or a running stream of water, in any case not with ice. Cover the affected area with clean cotton sheet or gauze. Do not attempt to remove the material from skin; it could result severe tissue damage. Get medical attention.
Ingestion: Not applicable
Inhalation: In case typical symptoms occur, remove the victim to fresh air. Get medical attention if symptoms persist.

5. Fire fighting measures

Flashpoint: > 340°C
Ignition conditions: Polyethylene is a combustible substance but under normal housekeeping conditions there is no risk of ignition. In contact with a flame it becomes soft, flows, ignites and burns with a light flame until exhausting (if it isn't stabilized with a flame retardant agent). Static electricity easy accumulates during handling/storage and may constitute an ignition source in case a high dust concentration exists.
Toxic combustion products: Carbon mono and dioxide, other oxidation organic compounds. In case of burning without sufficient oxygen, a black, dense smoke is released
Extinguishing media: Small fire: dry chemicals, and carbon dioxide extinguishers. Large fires: large quantities of water spray.
Fire fighting procedures: Keep people away. Isolate fire area and deny unnecessary access. Cool the area with water to localize the fire. Soak with water to cool and to avoid re-ignition.
Protective equipment for fire fighters: Complete fire fighting clothing, self-contained breathing apparatus. In case these are not available, fire extinguishing has to be done from a safe distance or a protected location. .
Explosion hazard: The product as delivered has no explosive character. In case of accumulation, polymer dust may form explosive mixtures with the air.

6. Accidental release measures

Personnel protection*:* Remove unnecessary personnel from area. Limit access to the area. Spilled pellets may induce slipping hazard. Molten polymer presents thermal burns hazard in case of skin contact.
Environment protection*:* The released material will not be discharged to the sewerage.
Clean up: The contaminated area shall be swept and cleaned, and the residual material collected in dried and labeled containers. For disposal, see section 13.

7. Handling and storage

Store polyethylene in dark, dry and well-ventilated area, away from all heat and ignition sources (sparks, open flames or hot surfaces, welding operations), combustible materials or incompatible substances (benzene, chlorophorm, decalin). Temperature in the storage area shall not exceed 40^0C. Avoid dust accumulation by frequent cleaning and suitable warehouses structure. Local exhaust ventilation is recommended for control of airborne dust, fumes and vapors, in enclosed areas.
During handling and processing, polymer may charge electrostatic. Use only machines fitted with earth.

8. Exposure control / personal protection

Eyes and hands protection: Safety glasses for handling at ambient temperature. Thermal resistant gloves, arm protection and goggles/face shield in case of possible contact with molten product.
Skin and body protection: In case of polymer handling or processing at elevated temperatures or in a molten state, adequate protective equipment will be used over the skin, to prevent contact.
Respiratory protection: For most conditions, no special respiratory protection is necessary. When polymer is heated, general and local ventilation systems will be provided.
Hygienic measures: Inside work areas, eating is not allowed. Normal clothing will be kept separately from work and protective equipment.

9. Physical and chemical properties

Physical state: Pellets, powder
Color: White translucent
Odor: No odor
Melting temperature: 130-160 °C
Flash point: > 340 °C
Density: 0.91 - 0.94 g/cm^3
Water solubility: Negligible

10. Stability and reactivity

Chemical stability: Polyethylene pellets are normally stable. The product is not corrosive.
Hazardous polymerization: No
Conditions to avoid: Excessive temperatures, sparks or open flames.
Materials to avoid: Solvent substances (benzene, chlorophorm, decalin).
Hazardous decomposition products: Carbon mono and dioxide, other oxidation organic products.

11. Toxicological information

Acute toxicity: Polyethylene is considered non-toxic for animals, in case of powder inhalation or solid swallowing.
Local effects: Unknown
Sensibility: Unknown
Chronic toxicity: Unknown
Cancer hazard: Not established
Maximum concentration accepted: Not regulated.
As a limitation, the dust level – according OSHA limits - must not exceed 15 mg/m^3 for total dust and 5 mg/m^3 for respirable dust. According ACGIH, the limit for total dust is 10 mg/m^3. If toxic impurities or decomposition products appear, it has to take into consideration the smallest limits stipulated in local or national legislation.

12. Ecological information

Movement: Soil- the product will not migrate. Water – the product will float.
Degradation: The product is inert and it is not biodegradable. Surface photo degradation is expected with exposure to sunlight. Due to the negligible water solubility, it produces no effects on aquatic environment.
Bioaccumulation: Not expected
Ecotoxicity: Minimal, due to the negligible water solubility. Pellets may be harmful for birds and fish if swallowed.

13. Disposal considerations

Spilled material removal: Sweep and clean contaminated area, collect residual material into dried, labeled containers. Wash the area with water.
Wastes disposal: Polyethylene is a recyclable material. It is preferably that production rejects and conversion wastes be recycled instead of being disposed.
Disposal of any wastes should respect all national and local valid regulations. If these regulations are met, the following is applicable for polyethylene, as supplied; additives, fillers or other materials addition involves their influence consideration, on the afferent documentation basis. Polyethylene can be disposed by landfill or controlled incineration, respecting valid regulations regarding gaseous or solid particles discharges. Due to the high heat value, incineration has to be done only in units designed to handle high heats of combustion. In case it is landfilled: polyethylene is inert, does not degrade quickly, form a strong and permanent soil base and does not release gases or other compounds known to pollute water resources.

14. Transport information

International settlements: not regulated by RID, ADR, DOT, IATA, ICAO, IMDG rules.

Polyethylene pellets transport: CP4 euro pallets (1375 kg LDPE/pallet, distributed in polyethylene bags, containing each one 25 kg of product), big-bags- in truck or rail silo, maritime transport containers
Polyethylene powder transport: polyethylene bags, containing each one 25 kg of product, big-bags- in truck or rail silo.

15. Regulatory information

According valid Romanian legislation:

Label:	**Hazard symbol:**	Not regulated
	R - phrases:	Not regulated
	S - phrases:	Not regulated

According international legislation: To the best of Rompetrol Petrochemicals knowledge, the product contains no chemical subject to SARA /Title III, OSHA or CERCLA requirements.

16. Other information

Rompetrol Petrochemicals does not recommend any company product for applications that involve human tissues or internal fluids contacts (regardless of the contact length of time), for cardiac devices, for medical device components that support human life, as well as for applications that have connections with human reproduction.

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The conditions or methods of handling, storage, use and disposal of the product are beyond our control and may be beyond our knowledge. For this, we do not assume responsibility for loss, damage, or expense arising out or connected with handling, storage, use or disposal of this product.

Price Plastics Pty Ltd

Material Safety Data Sheet

1. IDENTIFICATION OF THE MATERIAL AND SUPPLIER

Product Name	Microtuff® Polyethylene Powders
Company Name	Price Plastics Pty Ltd
Address	515 Hammond Road Dandenong Vic 3175
Telephone Number	(03) 8792 5300
Fax Number	(03) 9768 2536
Product Use	Polyethylene powders for use in rotational moulding applications Microtuff 6110UV, Microtuff 6050UV, Microtuff 6010UV Microtuff 6435UV, Microtuff 6440UV, Microtuff 8550UV, Sunsmart 6185UV, Microtuff 3499UV This MSDS does not cover specialty grades like foam or flame retardant PE.

2. HAZARDS IDENTIFICATION

Hazard Classification	Non-Hazardous Substance Non-Hazardous Goods

3. COMPOSITION AND INFORMATION ON INGREDIENTS

Chemical Characterization	Polyethylene Powder containing pigments and additives	
Ingredients	Name	Content
	Polyethylene + proprietary additives	95-100 %
	Pigment Masterbatch	0-5 %

4. FIRST AID MEASURES

Inhalation	Remove to fresh air. Seek medical advice if symptoms persist.
Ingestion	Rinse mouth with water. Give plenty of water to drink. Do not induce vomiting. Seek medical advice if symptoms persist.
Skin contact	If irritation occurs, wash contact area with soap and water. Molten material will adhere to skin and cause burns. Cool material as quickly as possible with water. Do not remove material or clothing from skin as this may result in further damage to the skin - see a physician for removal of the material and treatment of the burn.
Eye	If powder gets in the eyes, wash with copious amounts of water, holding eyelids open. Treat as skin burn if in contact with molten material. In all cases of eye contamination it is a sensible precaution to seek medical advice.
Fist Aid Facilities	Eye wash and normal washroom facilities
Advice to Doctor	Treat symptomatically. Advice as per above information.

5. FIRE FIGHTING MEASURES

Extinguishing Media	Carbon dioxide, foam, dry chemical, water fog or fine water spray
Unusual Fire and Explosion Hazards	High concentration of airborne powders, fines or dust may form explosive mixtures with air. Risk of dust explosion is increased if flammable vapours are also present. May accumulate hazardous static charge when agitated in transfer handling systems

Special Fire Fighting Procedures	Fire fighters must use self contained breathing apparatus. Gases evolved by burning polyethylene include carbon monoxide, carbon dioxide, low levels of acrolein, formaldehyde and other aldehydes, ketones, methane, ethane and acetylene.
Hazchem Code	n.a.
Decomposition Temp.	> 250°C

6. ACCIDENTAL RELEASE MEASURES

Spills and Disposal	Dampen down to prevent spread by wind. Shovel or sweep up spilled material and dispose of or recycle. Disposal of recovered material should conform to local regulations. If large quantities of this material enter the waterways, contact the Environmental Protection Authority or your local Waste Management Authority. NOTE: Spilled powder on surfaces and floors is a slip hazard and should be swept up immediately.

7. HANDLING AND STORAGE

Handling	Ensure good ventilation/exhaust at workplace. Avoid contact with eyes and skin. Avoid inhalation of dust. Due to dust explosion hazard, minimise the production of fines and dust when handling this product. Prevent build-up and concentration of fines/dust around equipment and on floors and surfaces such as ducting, structure beams and ceilings. Earth (ground) all material handling and transfer equipment to dissipate static electricity. Keep away from uncontrolled heat and other ignition sources.
Storage	Store in cool, dry area

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls	Good general ventilation is required under ordinary conditions of use. Avoid inhaling dusts and fumes generated during use. Use local exhaust ventilation during processing if required.
Personal Protective Equipment	Thermal resistant gloves should be worn when handling hot materials. Use safety glasses. Under dusty conditions or if fumes build up during processing, use approved respirators to AS/NZS1715 and AS/NZS1716 to avoid exposure by inhalation.
Other Exposure Information	No exposure standard has been published by the NOHSC. An 8 hour occupational exposure limit of 10 mg/m^3 for nuisance dusts is recommended.

9. PHYSICAL AND CHEMICAL PROPERTIES

Form	Solid
Appearance	Natural or coloured powder
Decomposition Temp.	> 250°C
Melting Point	100-140°C
Boiling Point	n.a.
Vapour Pressure	n.a.
Flash Point	n.a.
Flammability	Combustible solid. May form flammable dust clouds in air. Polymer may

	burn in presence of extreme heat and oxygen. Avoid extreme heat.
Auto Ignition Temp.	Approx. 350°C
Lower Flammability Limit	None allocated
Other Information	Density (range) 0.930 – 0.945 Water solubility: negligible

10. STABILITY AND REACTIVITY

Stability	Thermal, light, etc: stable
Conditions to avoid	Extreme heat
Incompatibility	Strong oxidising agents
Hazardous decomposition products	Carbon monoxide, aldehydes, acetic acid, ketones, acrolein, ethane, methane

11. TOXICOLOGICAL INFORMATION

Toxicology Information	Not available
Inhalation	Inhalation of dust may cause irritation of nose and throat. Fumes given off during processing can cause respiratory irritation, headache and nausea.
Ingestion	No known effects/minimal toxicity. May cause choking if swallowed. Large amounts may cause nausea and vomiting.
Skin	Prolonged skin contact may result in irritational rash. Contact with hot or molten product may cause burns.
Eyes	Molten product may cause burns. Fines and powder may scratch eye surfaces and cause mechanical irritation. Fumes given off during processing may cause eye irritation.
Chronic Effects	None known.

12. ECOLOGICAL INFORMATION

Environmental Protection	No data available

13. DISPOSAL CONSIDERATIONS

Disposal	Spilled or waste material should be recycled if possible, otherwise it must be disposed of in accordance with the applicable local, state and federal regulations.

14. TRANSPORT INFORMATION

U.N. Number	n.a.
Proper Shipping Name	n.a.
DG Class	n.a.
Hazchem Code	n.a.
Packing Group	n.a.
Storage and Transport	Keep containers closed and check regularly for spills. The products listed in this MSDS are not classified as dangerous goods in the Australian Dangerous Goods Code.

15. REGULATORY INFORMATION

	Not classified as hazardous according to NOHSC criteria.
Poisons Schedule	Not scheduled

Packaging and Labelling	No special requirements

16. OTHER INFORMATION

Manufacturers Advice	Conveying lines and equipment in material handling systems should be grounded to eliminate or reduce the build up of static electricity. Avoid sources of ignition where fines may occur.
Other Information	Since the specific conditions of use of this product are outside the control of the supplier, the user is responsible for ensuring that the requirements of relevant legislation are complied with. The information contained in this safety data sheet is correct to the best of our knowledge and information at the data of publication. The information relates only to the specific product(s) designated and may not be valid for the product if used in combination with other products or any processes other than those specified in the text.
Revision	02/08/2016

Environmental and Health Hazards of Chemicals in Plastic Polymers and Products

Delilah Lithner

Ph.D. thesis
Department of Plant and Environmental Sciences
University of Gothenburg

Faculty of Science

UNIVERSITY OF GOTHENBURG

Environmental and health hazards of chemicals in plastic polymers and products

Delilah Lithner, 2011

Department of Plant and Environmental Sciences

Faculty of Science

UNIVERSITY OF GOTHENBURG

Doctoral thesis for the degree of doctor of Philosophy in Natural Science, specialising in Environmental Science

The thesis will be publicly defended Friday 6th May, 2011, at 10 a.m., in Hörsalen, Department of Plant and Environmental Sciences, Carl Skottbergs gata 22 B, Göteborg.

Faculty opponent: Professor Christina Rudén, KTH Royal Institute of Technology, Stockholm.

Examiner: Professor Hans Blanck, Plant and Environmental Sciences, University of Gothenburg.

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Department of Plant and Environmental Sciences
University of Gothenburg, Sweden

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Abstract

Plastics are extremely diverse in terms of chemical composition, properties and possible applications, and are widely distributed in the society and the environment. In the last 15 years the global annual production has doubled, reaching 245 million tons in 2008. Several of the chemicals used to produce plastics are hazardous for human health and the environment. These, and their degradation products, may be released during the life cycle of a plastic product. The plastic polymers are not considered as toxic, but in plastic products there may be non-bound residual monomers, polymerisation chemicals, degradation products, and additives which have toxic properties.

The overall aim of this thesis, which is based on five papers [I-V], was to study the environmental and health hazards of chemicals in plastic polymers and products. Leaching tests, toxicity tests and Toxicity Identification Evaluations (TIEs) were made on plastic products [I, II], synthetic textiles [III], and discarded electronic products [IV]. A hazard ranking model was developed and used to rank plastic polymers based on monomer composition and environmental and health hazard classifications [V]. Also other hazardous substances needed to produce each polymer were identified [V].

Substances causing acute toxicity to *Daphnia magna* (water flee) leached from one third of all 83 plastic products/textiles even during short term (1-3 d) leaching in deionised water [I-III]. The toxic leachates came mainly from products that were soft to semi-soft, i.e. plasticised PVC (11/13) and polyurethane (3/4), and from epoxy products (5/5), and from synthetic textiles made of various plastic fibres [I-III]. The electronic product leachates that were acutely toxic came from mixed material and metal components, and not from plastics components. TIEs, performed on some leachates, indicated that the major toxicants were hydrophobic organics for the plastic product and synthetic textile leachates [I-III], and metals for the electronic product leachates [IV].

The polymers ranked as most hazardous are made of monomers classified as mutagenic and/or carcinogenic (category 1A or 1B). These belong to the polymer families of polyurethanes, polyacrylonitriles, PVC, epoxy resins, and styrenic copolymers (ABS, SAN and HIPS), and have a large global production (1-37 million tons/year). A considerable number of polymers, 31 out of 55, are made of monomers that belong to the two highest of the ranking model's five hazard levels [V]. Examples of such polymers, with a large global production (1-5 million tons/year), are phenol formaldehyde resins, unsaturated polyesters, polycarbonate, polymethyl methacrylate, and urea-formaldehyde resins [V].

The ranking model was useful for identifying and comparing hazardous substances, and the results from the hazard identification can be used for further hazard and risk assessment for decisions on the need for risk reduction measures, substitution or phase out.

In conclusion, considering the extensive dispersion in the society and the environment, the growing production, and the release and use of many hazardous chemicals, it is important to further assess the risks of chemicals associated with plastic polymers and products.

Key words: plastics, plastic products, plastic polymers, consumer products, environmental hazards, environment, health hazards, human health, hazard ranking, hazard assessment, chemical ranking, hazard identification, hazardous chemicals, emissions, toxic substances, toxicity, acute toxicity, aquatic toxicity, *Daphnia magna* Toxicity Identification Evaluation, TIE, leaching, leachates, product leachates

Sammanfattning (Summary in Swedish)

Plastmaterial uppvisar en stor mångfald i kemisk sammansättning, egenskaper och användningsområden, och har en stor spridning i samhället och i miljön. De senaste 15 åren har den globala årsproduktionen fördubblats, till 245 millioner ton år 2008. Flera av kemikalierna som används för att tillverka plast är skadliga för människors hälsa och miljön. Dessa, eller deras nedbrytningsprodukter, kan avges under en plastprodukts livscykel. Plastpolymererna är inte betraktade som toxiska, men i plastprodukterna kan det finnas icke-bundna restmonomerer, polymerisationskemikalier, nedbrytningsprodukter och additiv som har toxiska egenskaper.

Det övergripande syftet med denna avhandling, som baseras på fem artiklar [I-V], var att studera miljö- och hälsofarorna av kemikalier i plastpolymerer och produkter. Laktester, toxicitetstester och toxicitetsindentifiering (TIE) utfördes på plastprodukter [I, II], syntetiska textilier [III] och uttjänta elektroniska produkter [IV]. En farorankningsmodell utvecklades och användes för att rangordna plastpolymerer med avseende på deras kemiska beståndsdelar (monomerer) och miljö- och hälsofaroklassificeringar [V]. Även andra miljö- och hälsofarliga kemikalier som behövs för att tillverka respektive polymer identifierades [V].

En tredjedel av alla 83 plastprodukter/textilier släppte ifrån sig ämnen som orsakade akut toxicitet för *Daphnia magna* (vattenloppa), trots att lakningen pågick under kort tid (1-3 dygn) i avjoniserat vatten. De toxiska lakvattnen kom huvudsakligen från produkter som var mjuka till halvmjuka, d v s mjukgjord PVC (11/13) och polyuretan (3/4), och från epoxiprodukter (5/5), och från textilier gjorda av olika plastfibrer [I-III]. Elektronikprodukternas toxiska lakvatten kom från metall- eller blandmaterialfraktionen, inte ifrån den rena plastfraktionen [V]. Toxicitetsindentifieringen, som utfördes på några av lakvattnen, indikerade att giftigheten huvudsakligen orsakades av hydrofoba organiska ämnen för plastprodukterna och de syntetiska textilierna [I-III], och av metaller för elektronikprodukterna [V].

De högst farorankade polymererna är gjorda av monomerer som är klassificerade som mutagena och/eller cancerogena (kategori 1A och 1B). Dessa tillhör polymerfamiljerna polyuretaner, polyakrylonitriler, PVC, epoxiplast och styrensampolymerer (ABS, SAN och HIPS), och har en hög global produktion (1-37 miljoner ton/år). Ett betydande antal polymerer (31 av 55) är gjorda av monomerer som tillhör de två högsta av farorankningsmodellens fem faronivåer [V]. Exempel på sådana polymerer, som dessutom har en hög global produktion (1-5 miljoner ton/år), är fenolformaldehyd, omättad polyester, polykarbonat, polymetylmetakrylat och ureaformaldehyd. Farorankningsmodellen var ett bra verktyg för identifiering och jämförelse av farliga kemikalier, och resultaten från faroidentifieringen kan användas för fortsatt riskbedömning inför beslut om behov av riskminskningsåtgärder, substitution eller utfasning.

Sammanfattningsvis är det viktigt att ytterligare bedöma riskerna av kemikalier som rör plastpolymerer och plastprodukter, inte minst p g a den stora spridningen i samhället och miljön, den ökande produktionen, och användningen av många farliga kemikalier.

Sökord: plast, plastprodukter, plastpolymerer, konsumentprodukter, miljöfaror, miljö, hälsofaror, hälsa, farorankning, kemikalierankning, faroidentifiering, farobedömning, farliga kemikalier, utsläpp, giftiga ämnen, toxicitet, akut toxicitet, akvatisk toxicitet *Daphnia magna*, toxicitetsidentifiering, TIE, lakvatten, produktlakvatten

List of papers

This thesis is based on the following papers:

I. Lithner, D., Damberg, J., Dave, G., Larsson, Å., 2009. Leachates from plastic consumer products – Screening for toxicity with *Daphnia magna*. *Chemosphere 74, 1195-1200.*

II. Lithner, D., Nordensvan, I., Dave, G., 2011. Comparative acute toxicity of leachates from plastic products made of polypropylene, polyethylene, PVC, acrylonitrile-butadiene-styrene and epoxy to *Daphnia magna. Submitted.*

III. Lithner, D., Ivåker, J., Dave, G., 2011. Comparative acute toxicity of leachates from synthetic textiles made of plastic fibres to *Daphnia magna*. *Manuscript.*

IV. Lithner, D., Halling, M., Dave, G., 2011. Toxicity of electronic waste leachates to *Daphnia magna* - Screening and Toxicity Identification Evaluation of different products, components and materials. *Submitted.*

V. Lithner, D., Larsson, Å., Dave, G., 2011. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Submitted.*

The papers are referred to by their Roman numerals. These papers appear after the summarizing chapter of this compilation thesis. For paper V supplementary materials (Report S1 and Table S1) are provided at the end of the thesis.

Contents

1. Introduction

Humans, animals, plants, and microorganisms are exposed to a very large number of chemicals that are released from many different sources and may enter the organisms by different routes. Many of these chemicals may not cause harm individually, if they occur in low concentrations, but the combination effects from exposure to all these chemicals, even at low concentrations, during a prolonged period of time, may lead to adverse effects for human health and the environment.

Chemical diversity, abundance and hazardousness are one of the major environmental challenges of today. On the contrary to biological diversity, chemical diversity can be problematic from an environmental point of view. There is not sufficient knowledge to provide protection for human health and the environment against all these chemicals, which according to the European Inventory of Existing Commercial Chemical Substances (EINECS) is slightly above 100.000 (Ex ECB, 2011).

Plastic polymers and products, which are the focus of this thesis, are extremely diverse, both in terms of chemical composition, properties and possible applications. Several hazardous substances may be released during the life cycle of a plastic product; and considering the large and growing global consumption of plastic products, and their omnipresence and persistence in the environment, there is a need for assessing the hazards and risks of this large material group.

The overall aim of this thesis was to study the environmental and health hazards of chemicals in plastic polymers and products from a toxicological perspective.

1.1. Plastics in the society

Production of plastic materials started on an industrial scale in the1940s and 1950s. In the last 15 years the global annual production of plastics has doubled, reaching 245 million tons in 2008 (calculated from PlasticsEurope, 2009). The annual plastic material consumption per capita in Western Europe, Canada, USA and Mexico, was 100 kg in 2005, which was ten times as much as African countries and five times as much as Asian countries, excluding Japan (PlasticsEurope, 2009). This means that there is a large potential for further increased consumption.

The world plastic demand is dominated by the thermoplastic types polypropylene (21%), low- and linear low-density polyethylene (18%), polyvinyl chloride (17%), and high-density polyethylene (15%). Other plastic types with high demand are polystyrene and expandable polystyrene (8%), polyethylene terephthalate, PET (7%, excluding PET fibre), and the thermosetting plastic polyurethane (6%; figures for 2007; Plastics Europe MRG, 2008).

Plastic polymers are not only used to make plastic products but also to make synthetic fibres, foams, coatings, adhesives and sealants, which are used in numerous applications, both indoors and outdoors. The synthetic fibres account for an additional 40 million tons/year (figures for 2009; Engelhart, 2010). In Europe the use of plastics is dominated by packaging (38%), followed by building and construction (21%), automotive (7%), electrical and electronic (6%), and other sectors (28%) such as medical and leisure (PlasticsEurope, 2009). Plastic use is dominated by single use or short term use, and at the same time most plastics are extremely persistent in the environment.

Plastics are important in our society and offer many benefits for human health and the environment, for instance (PlasticsEurope, 2009; Andrady and Neal, 2009):

- Plastic packaging protects food and goods from getting wasted and/or contaminated and thereby saves resources.
- The light weight packaging material (due to high strength-to-weight ratio) saves fuel and decreases emissions during transportation.
- Plastic water supply systems and storage containers/tanks provide clean water.
- Light plastic materials (replacing metals) in cars and aircraft save fuel and decreases emissions.
- Efficient plastic insulation materials in buildings save energy and provide climate protection.
- Plastic protective clothing and safety equipment (e.g. fire proof materials, helmets, air bags) protects form injury.
- Plastic products for medical applications are very important and contribute to improved heath (e.g. blood pouches, tubings, disposable syringes, prosthesis).
- Solar heaters and solar panels, in parts made of plastics, provide renewable energy.

1.2. Plastics in the environment

Consumption, of course, leads to waste, and in the case of plastics, large volumes of extremely persistent waste are created. The problems with plastic waste are many.

1.2.1. Plastic waste management

The largest plastic waste fraction goes to landfill. For Europe the average is around 50% (Plastics Europe, 2009). Landfill space is scarce in many countries which leads to emissions from transportation over long distance, and increasing the landfill area may require valuable land. Emissions from landfills may also contaminate ground and surface water. Alternatives to landfilling are mechanical recycling, energy recovery, or chemical recovery. The heterogeneity of plastic products and types obstructs recycling, or makes plastic recycling difficult in many cases (Hopewell, 2009). Recycling is possible for some fractions, but in order to get a similar, or not a too low grade product, a homogenous fraction is required, which requires labour intensive sorting. Plastic waste for recycling is often transported over long distances, for instance exported from the industrial to the developing countries, particularly in Asia (PlasticsEurope, 2010). Energy recovery by incineration of plastic waste in Europe has a larger share (30 %), than recycling (20%) (PlasticsEurope, 2009). Combustion of plastics may cause emissions of hazardous substances and contributes to global warming (since most plastics are fossil based). Chemical recovery is under development and means that chemicals, e.g. raw materials such as monomers and gases, are recovered/converted from the plastic material. This can, for instance, be done by controlled thermal degradation such as thermolysis, which is a non-catalytic cracking process (Al-Salem, 2009).

Some solutions to plastic waste and recycling problems have resulted in new uses for plastic waste, and sometimes even more chemically complex products are created, and further dispersion in the environment may follow. For instance in Bangalore, India, plastic asphalt is used as an alternative road material. The asphalt is made from churned plastic waste (mainly composed of plastic bags, PET bottles and thin plastic film) which is blended with bitumen. (Khullar, 2009; Gulati, 2010). The roads are expected to last for 4-6 years, and the end of life management is not described.

1.2.2. Plastic waste in the marine and terrestrial environment

A very large fraction of plastic waste ends up as litter in the terrestrial and marine environment. The marine environment is especially exposed and has been most widely studied. Large and increasing amounts of plastic products, debris, fragments and even micro-particles are found in the open ocean, on the surface, in the deep ocean and ocean bed, in coast lines, in sediments, and in organisms (Barnes et al., 2009; Thompson et al., 2004). The sources are not solely from dumping at sea, but a large quantity is likely to come from land sources, e.g. littering on land (especially coastal areas), plastics blown from landfill sites, and sewage effluents, as well as spillage during transport and accidents (Barnes et al., 2009). This plastic waste can be transported far by currents, for instance the great oceanic gyres (Yamashita, 2007). It can also accumulate in the centre of the gyres, as shown by e.g. Moore (2001; 2008) and Lavender Law et al. (2010). The plastic products and debris are fragmented into smaller pieces, even to sizes below 5 mm, called microplastics (Barnes et al., 2009).

Plastic fragments in the marine environment have been reported in scientific reports since the late 1960s (reviewed by Barnes et al., 2009). However, the extent of this plastic pollution, especially by microplastics, is much more prevalent than previously thought, both in terms of greater quantities and smaller particles. For instance, in surface trawl studies (net mesh size 330 μm) plastics were found at 55 of 76 locations in the Kuroshio Current area (North Pacific), in quantities ranging $0–3.52 \times 10^6$ pieces/km^2, with a mean abundance of 1.74×10^5 pieces/km^2 (Yamashita, 2007); and near the central pressure cell of the North Pacific subtropical high a mean abundance of 3.34×10^5 plastic pieces/km^2 were found (Moore et al., 2001). The particle sizes 1-3 mm constituted 62% of all marine plastic pieces (Yamashita, 2007). Even smaller sizes of plastic pieces ≤20 µm in sediment have been reported by (Thompson et al., 2004; Ng and Obbard, 2006).

Effects from entanglement or ingestion of plastic waste, including suffocation or blocking of digestive tract causing death, have been well documented for birds, turtles, and marine mammals (reviewed by Gregory, 2009). The consequences of exposure to microplastic in filter feeding organisms and deposit feeders are not yet known. Studies of exposure to microplastics in amphipods, lugworms, barnacles, sea cucumbers, and mussels have shown that the organisms ingest the microplastics (Thompson et al., 2004; Graham and Thompson, 2009; Browne et al, 2008). Further studies on the mussels showed that the microplastics were translocated from the gut to the circulatory system and were found in the hemocytes (blood cells; Browne et al., 2008).

The ability of plastics to sorb persistent organic pollutants may cause additional problems. In marine polypropylene pieces Mato et al. (2001) found 100.000 to 1 million times higher concentrations of PCBs (polychlorinated biphenyls) and DDE (dichlorodiphenyl-dichloroethylene) than in the surrounding seawater. If these pollutants are released when ingested by an organism remains to be investigated. Marine plastics can also be vectors for transport of sessile alien invasive species (Barnes, 2005) and may cause damage to ecosystems.

1.2.3. Plastic degradation

The persistence of plastic waste is another problem. Most plastic polymer types are resistant to biodegradation, i.e. degradation by microorganisms, and the two most abundant ones, polyethylene and polypropylene, are extremely resistant to biodegradation (Nicholson, 2006). In a polyethylene polymer only 0.1% of the carbon will be transformed into CO_2 per year by biodegradation under optimal laboratory exposure conditions, according to Andrady (1998). There are a few biodegradable plastics which today only have a minor, but growing, share in the plastic market. Not all of them, however, are completely biodegradable in the natural environment (Rudnik, 2008; O´Brine and Thompson, 2010).

Non-biodegradable polymers can be degraded by heat, oxidation, light, ionic radiation, hydrolysis and mechanical shear, and by pollutants such as carbon monoxide, sulphur dioxide, nitrogen oxide and ozone (Ravve, 2000). This causes the polymer to get brittle, to fragment into small pieces and to release degradation products. Different degradation mechanisms exist and which of them that will dominate depends on the polymer type. Chain scission involves breaking the chemical bonds in the polymer molecule, and is often random, but for some polymers it proceeds at the polymer end chains and the initial monomers are broken off, a process called depolymerisation (Alger, 1997; Braun, 2005). Another degradation mechanism is chain stripping in which the side atoms/groups attached to polymer main chain are released; usually these are volatile molecules (Wilkes, 2005). Crosslinking can also occur for some polymers and bonds are then created between the polymer chains (Wilkes, 2005). Complete conversion of the plastic product and its breakdown products, into carbon dioxide, water and inorganic molecules by photo- and biodegradation (Gregory and Andrady, 2003), is for most plastic types extremely slow (Innocenti, 2003). In the marine environment degradation is especially slow, since degradation mainly is likely to occur by solar radiation and slow thermal oxidation (Gregory and Andrady, 2003). This means that the time frame for complete degradation is very long and could, in some situations, be several hundred years.

1.3. Regulations for hazardous chemicals in articles/plastic products

The European chemicals legislation, REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) aims to improve the protection of human health and the environment through an earlier and improved identification of the intrinsic properties of chemical substances (European Commission, 2011a). Provisions are laid down for substances and preparations and shall also apply to the use of these chemicals in articles (European Parliament and Council, 2006) and, thereby, to some extent cover chemicals in articles. For the finished article the requirements are not as far reaching as for single substances and preparations. Monomers and polymers are less strictly regulated than other chemicals, since there are some exemptions from the general requirements in REACH (ECHA, 2008).

However, in the European Union there are restrictions for use and even bans for some substances in certain product groups. The ones applicable to plastics and plastic products are for instance:

- The phthalate plasticisers DEHP (di(2-ethylhexyl) phthalate), DBP (dibutyl phthalate) and BBP (benzyl butyl phthalate) in toys and child care articles, at concentrations >0.1% by mass (European Parliament and Council, 2006).
- The phthalate plasticisers DINP (diisononyl phthalate), DIDP (diisodecyl phthalate) and DNOP (di-n-octylphthalate) in toys and child care articles which can be placed in the mouth (concentrations >0.1% by mass; European Parliament and Council, 2006).
- Cadmium for giving colour to plastics, or used as stabilisers in PVC (European Parliament and Council, 2006).
- The flame retardants polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE) in electronic products (RoHS-directive; European Parliament and Council, 2003).
- Bisphenol A in baby bottles (from 1st March 2011; European Commission, 2011b).

Recently (17 February 2011), the European Commission announced a ban on use of six substances which is to be effective within three to five years, unless an authorisation has been granted to individual companies for their use (European Commission, 2011c). Four of them are used in plastics, i.e. the phthalate plasticisers DEHP, BBP and DBP, mainly used in PVC, and 4,4'-methylenedianiline (MDA) used as a curing agent for epoxy resins.

Also by international conventions there are regulations of use for certain substances. The Stockholm Convention on Persistent Organic Pollutants (POPs) requires the parties of the convention to eliminate or reduce the use of the listed POPs. Of the chemicals used in plastics some of the brominated flame retardants are listed. These include the polybrominated diphenyl ethers tetra-, penta-, hexa-, hepta-, and octaBDE and the polybrominated biphenyl hexaPBB (Secretary-general UN, 2009; UNEP, 2001).

The European Stabilizer Producers Association has made a voluntary commitment to replace lead stabilisers in PVC in the EU member countries by 2015 (Vinyl 2010, 2011).

There are no general requirements on release of hazardous chemicals from plastic products or for testing release, but there are some requirements for certain product groups. For instance, for plastic food contact materials there are EU directives which e.g. regulate migration levels and lists permitted additives (European Commission, 2011d). There is also a directive laying down the basic rules necessary for testing migration (release) from plastic materials and articles intended to come into contact with foodstuffs (European Council, 1982).

1.4. Plastic composition and hazardous chemicals

Plastic products are made from plastic polymers to which additives are added to enable processing and/or to give certain desired properties for a specific application (OECD, 2004). The polymers are made by polymerising monomers into macromolecular chains. These monomers are almost exclusively derived from non-renewable crude oil. Approximately 4% of world oil demand is used as raw materials for plastic production (British Plastic Federation, 2011).

Other substances (besides monomers) are often needed for polymerisation to occur, for instance initiators, catalysts, and depending on manufacturing process, solvents may also be used. The resulting plastic polymer can be blended with different additives, for instance plasticisers, flame retardants, heat stabilisers, antioxidants, light stabilisers, lubricants, acid scavengers, antimicrobial agents, anti-static agents, pigments, blowing agents and fillers, and is finally processed into a plastic product. There are many different plastic polymers and several thousand different additives, which results in an extremely large variation in chemical composition of plastic products (Rosato, 1998).

Plastic polymers are not particularly reactive and their large size limit transport across biological membranes (Anastas et al, 2000). They are, therefore, not considered as toxic. In the polymeric material, however, non-polymeric components such as residual monomers, oligomers, low molecular weight fragments, catalyst remnants, polymerisation solvents and a wide range of additives can be present (Crompton, 2007). Several of these are hazardous to human health and the environment, for instance carcinogenic, mutagenic, toxic for reproduction, sensitising and hazardous to the aquatic environment with long lasting effects. Since the non-polymeric compounds usually are of low molecular weight and are either weakly bound or not bound at all to the polymeric macro-molecules, they, or their degradation products, can be emitted from the plastic product (Crompton, 2007; OECD, 2004) to air, water or other contact media (e.g. food).

The content of non-polymeric substances varies between different plastic polymers and products. The residual monomer content depends on polymer type, polymerisation technique and techniques for reducing residual monomer content (Araújo, 2002). The contents presented for various polymers, in a review by Araújo (2002), was shown to vary from no or very low levels (100 ppm) to up to 40.000 ppm (i.e. 0.0001-4%). Also the amount of additives used is highly variable. PVC is the plastic type that requires by far the most additives. Of the world production of additives PVC alone accounts for 73% by volume, polypropylene and polyethylene account for 10 %, and styrenics account for 5% (Murphy, 2001).

Many additives are hazardous for human health and the environment. Some are especially hazardous, for instance brominated flame retardants used to retard ignition and prevent fire from spreading; some phthalate plasticizers mainly used to make PVC flexible; and lead heat stabilizers used to prevent degradation of PVC during processing (Murphy, 2001). Several polybrominated flame retardants are very persistent, very bioaccumulating and toxic, and are listed in the Stockholm Convention on Persistent Organic Pollutants (POPs) (Secretary-general UN, 2009). Among the phthalate plasticisers the most hazardous ones, i.e. BBP, DEHP and DBP, are classified as toxic for reproduction (category 1B). BBP is also very toxic to aquatic organisms with long lasting effects (European Parliament and Council, 2008; European Commission, 2009). In addition, these phthalates, as well as DEP (diethyl phthtalate) and DCHP (dicyclohexyl phthalate), are being evaluated for endocrine disrupting properties (Groshart and Okkerman, 2000; Okkerman and van der Putte, 2002). The lead compounds used in heat stabilizers are classified as toxic for reproduction (category 1A), very toxic to the aquatic environment with long lasting effects (both acute and chronic), and may cause damage to organs (European Parliament and Council, 2008).

1.5. Release and fate

Release of chemicals associated with plastic products may occur in all phases of the life cycle, i.e. during production, use, and end-of-life (Figure 1). The environmental fate of the polymer and of the substances released during the life cycle, including the degradation products, as well as the bioaccumulation potential, will affect the exposure for humans and the environment. The physical chemical properties of these substances, e.g. boiling point, vapour pressure, water solubility, and octanol-water partition coefficient, can be used to predict the environmental fate and bioaccumulation potential of these substances. Since plastic products are composed of many different chemicals, and the main part of these broken down into something completely different, this complicates the predictions.

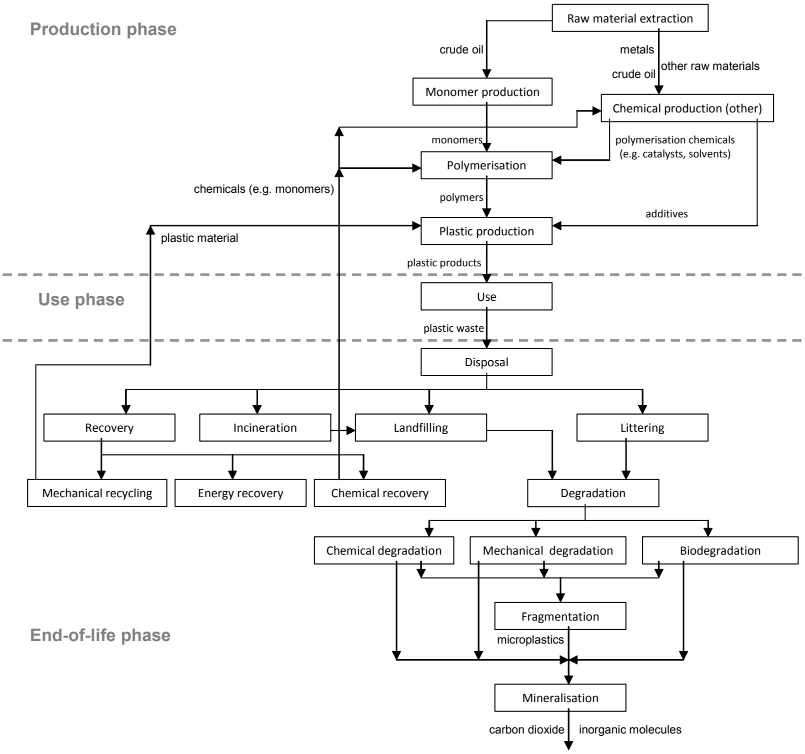

Figure 1. The life cycle of a plastic product (excluding energy input and emissions).

1.5.1. Release and release potential

The data of emissions to air and water from production of monomers, polymers and plastic products are very scarce. In EU risk assessment reports available for some of the monomers, there are a few emission data from polymer production. These data show varying emissions between different production sites and different polymers (European Commission (JRC), e.g. 2002a; 2002b; 2004; 2010).

Release of hazardous substances from plastic products to air, extraction fluids, water, food, food simulants, saliva and sweat have been shown by chemical analysis. Examples of substances studied and released from various plastic products include phthalates (Rijk and Ehlert, 2001; Tønning et al., 2010), brominated flame retardants (Kim et al., 2006), bisphenol A (Brede et al., 2003; Geens et al., 2010; Sajiki et al., 2007; Olea, 1996), bisphenol-A dimethacrylate (Olea, 1996), lead, tin and cadmium (Al-Malack, 2001), formaldehyde and acetaldehyde (Mutsuga et al., 2006; Özlem, 2008), 4-nonylphenol (Fernandes et al., 2008; Loyo-Rosales et al., 2004), MTBE (methyl tert-butyl ether), benzene (Skjevrak, 2003) and many other volatile organic carbons (Henneuse-Boxus and Pacary, 2003; Lundgren et al., 1999). In several of the mentioned studies the released concentrations are low (e.g. compared to guideline values), but in others they are considerably higher.

The size and type of emissions from plastic products are controlled by many factors. The content of non-polymeric substances controls what can be released, while other factors control the potential of release into a surrounding medium, i.e. the migration potential. Migration is generally favoured if the polymer matrix is permeable; if the size of gaps between polymer molecules is larger than the size of migrant; if the migrant is small, has a similar solubility parameter as the polymer and is volatile; if the temperature is high; and if the surrounding medium is water for water soluble migrants, fat containing for hydrophobic migrant and acidic for metals (Brydson, 1999; Sheftel, 2000).

1.5.2. Degradation products

The degradation products formed during degradation (described in 1.2.3.) will vary depending on polymer type (Ravve, 2000). The type and quantity of degradation products formed may also be influenced by degradation mechanisms, presence of polymerisation impurities, and surrounding factors, e.g. temperature and oxygen (La Mantia, 2002; Ravve, 2000). During thermal degradation nitrogen-containing plastics (e.g. nylons, polyacrylonitrile, and polyurethanes) release hydrogen cyanide; chlorine-containing materials (e.g. PVC) release hydrogen chloride; and fluorine-containing polymers (e.g. polyvinylidene fluoride and PTFE) release hydrogen fluoride by a chain stripping mechanism (Fardell, 1998; Lokensgard and Richardson, 2003; Ravve, 2000). Polymers capable of depolymerisation by chain scission include polymethyl metacrylate, polytetrafluoroethylene, and polyoxymethylene, which can depolymerise completely into their initial monomers. Also polystyrene, polyesters (e.g. PET and polycarbonate), nylons and polyurethanes can depolymerise to some extent into their monomers (Alger, 1997; Ravve, 2000; Allen and Edge, 1992; La Mantia, 2002). All plastic types emit carbon monoxide and carbon dioxide upon burning (Fardell, 1998).

1.6. Exposure

For workers in the plastics industry the main route of exposure to toxic substances is by inhalation and absorption through the lungs, which according to Lokensgard and Richardson (2004) accounts for nearly 90 percent of the toxic symptoms observed in the plastics industry. This is quite expected since many of the hazardous chemicals used in plastic production are volatile organic compounds (VOCs). The VOCs are mainly emitted during the production phase, but also during the use and the end of life phase. This causes indoor air pollution which may be harmful for human health. VOCs also contribute to elevated ground-level ozone levels which may damage vegetation, can irritate the respiratory system, aggravate asthma and lung diseases, cause permanent lung damage, and affect the immune system (US EPA, 2011).

For consumers exposure to chemicals released from a plastic material during the use phase may vary greatly between different products. The exposure may for instance come from indoor air, food, water, and skin contact, but in most cases this is not likely to be so large that it will result in adverse effects. However, the actual exposure does not come from only one product but from a whole array of different plastic products, and exposure to a mixture of chemicals will often be continuous. Chemicals used in plastics have been detected in humans. Mainly presence of phthalates and bisphenol A, (reviewed by Koch and Calafat, 2009) and brominated flame retardants (Thomsen et al., 2010) have been studied. The main part of available research on chemicals associated with plastics is focusing on these substances.

Some consumer categories are particularly sensitive to hazardous chemicals, for instance infants, and larger margins of safety are, therefore, required. In Canada (2008) and the EU (2011), baby bottles made of polycarbonate have been banned because of the risk of bisphenol A leaching from the bottle. Bisphenol A has, within the EU strategy on endocrine disruption, preliminary been assigned category 1 based on evidence on human effects and high level of concern due to the risk of exposure, and is subject for evaluation for endocrine disrupting properties (Groshart and Okkerman, 2000).

At the same time, epoxy lining is promoted, and also used in some countries, as a very cost efficient alternative to re-piping in drinking water supply systems (Selvakumar et al., 2002). Epoxy lining means that the epoxy resin is injected and blown through to the piping system to prevent leaks and increase service life (Selvakumar et al., 2002). The most important epoxy resin (>80% of the market) is made from bisphenol A and epichlorohydrin (Gnanou and Fontanille, 2008). Both substances are classified as skin sensitizing, and epichlorohydrin is, in addition, classified as carcinogenic (category 1B). Migration of bisphenol A into food from epoxy lined cans have been shown (e.g. Sajiki et al., 2007; Geens et al., 2010).

Few data on measured environmental concentrations of plastic chemicals exist. In the EU drinking water directive the only parametric (limit) values related to plastic are for vinyl chloride, epichlorohydrin and metals (European Council, 1998). In the Swedish environmental monitoring program some of the plastic chemicals are included or have been screened, e.g. brominated flame retardants, phthalates, bisphenol A, and organotin compounds (Swedish EPA, 2007). Predictions of environmental concentrations (PEC) can be done for selected hazardous chemicals used in plastics.

1.7. Effects

Effects from chemical exposure can be studied from a human toxicological perspective and an ecotoxicological perspective. For the laboratory studies in this thesis aquatic ecotoxicological tests have been used to study effects.

In the field of ecotoxicology there are many ways to study effects of chemicals by using biological assays. This can be done by using:

- laboratory tests or field studies,
- *in vivo* (within a living organism) tests, which is most common, or *in vitro* (isolated organ, tissue, cell or biochemical system) tests,
- acute or chronic tests on a variety of test organisms (aquatic or terrestrial),
- species representing one or several trophic levels,
- single species or communities,
- various toxic endpoints to study different effects,
- standardised test procedures or test procedures adapted to a specific exposure scenario or ecosystem.

As all approaches have their pros and cons and none of them, of course, cover all aspects, it is important to be aware of the limitations with the chosen method when making assessments and predictions.

The simplest and least time consuming tests are usually aquatic acute toxicity tests in laboratory on bacteria, algae or small invertebrates. These show the effect of short term exposure, in terms of e.g. inhibition of growth, immobility or death, and require presence of toxicant(s) in relatively high concentrations. These tests can be advantageous for screening purposes, especially when the chemical composition of the test medium is not known, and thereby not either the anticipated toxic response. Chronic tests are usually more sensitive and ecologically relevant, since exposure to toxicants in the environment usually occurs in lower concentrations during a longer time period. Examples of other toxic effects include carcinogenicity, reproductive toxicity, mutagenicity, and various effects caused by endocrine disruption.

Many of the chemicals that are used to make plastic polymers and plastic products have been tested for toxicity to a varying extent, and the assembled data have provided the basis for harmonised environmental and/or health classifications for these substances. In paper V these hazard classifications are used to identify the potential environmental and health hazards associated with each plastic polymer type. The knowledge of effects from exposure to the mixture of substances that may be released from complexly composed plastic products is very limited. There are some toxicity studies made on different plastic materials. Most of them have been made on rodents exposed, by oral route, to either plastic powder or extracts from the plastic material. These studies, which mainly are in Russian, have been summarized and translated by Sheftel (2000) and they show toxic effects for some of the materials and no effects for others.

Few studies combining leaching tests with toxicity tests have been performed on plastic products. In this thesis acute toxicity of plastic product leachates are shown [I-III]. In another study, mudsnails cultivated in PET mineral bottles doubled their reproductive output, due to endocrine disruption, compared to those cultivated in Borosilicate Erlenmeyer flasks (Wagner and Oehlmann, 2009). In a study by Olea (1996), saliva samples collected after treatment with restorative dental filling composites (which are made from thermosetting acrylic composite bis-GMA) contained bisphenol-A and bisphenol-A dimethacrylate. The saliva samples were estrogenic in cell proliferation tests, compared to no estrogenicity in the saliva collected prior to filling.

1.8. Hazard and risk assessment

Hazard and risk assessments are used to assess the environmental and/or health hazards and risks of chemicals. Below hazard and risk assessment terminology is presented according to the harmonised definitions made by International Programme on Chemical Safety (IPCS, 2004). The definitions are very slightly paraphrased, and “agent or situation” is replaced with “chemical”.

A ***hazard*** is the inherent property of a chemical having the **potential to cause adverse effects** when an organism, (sub)population, or ecosystem is exposed to that chemical.

A ***risk*** is the **probability of an adverse effect** in an organism, (sub)population, or ecosystem caused under specified circumstances by exposure to a chemical.

Hazard assessment is a process designed to **determine the possible adverse effects** of a chemical to which an organism, (sub)population, or ecosystem could be exposed. It includes two steps:

1. ***Hazard identification*** is the identification of the type and nature of adverse effects that a chemical has an inherent capacity to cause in organism, (sub)population, or ecosystem.
2. ***Hazard characterization*** is the qualitative and, if possible, quantitative description of the inherent property of a chemical having the potential to cause adverse effects. If a quantitative description is possible it should include a dose–response assessment and its strengths and weaknesses.

Risk assessment is a process intended to calculate or **estimate the risk** to a given target organism, (sub)population, or ecosystem **following the exposure** to a chemical. A risk assessment includes four steps, of which the first two are from the hazard assessment:

1. Hazard identification
2. Hazard characterization (related term: Dose–response assessment),
3. ***Exposure assessment*** is the evaluation of the exposure of an organism, (sub)population, or ecosystem to a chemical (and its derivatives).
4. ***Risk characterisation*** is the qualitative and, if possible, quantitative determination of the probability of known and potential adverse effects of a chemical to occur in a given organism, (sub)population, or ecosystem, under defined exposure conditions.

Hazard and risk assessment methods, e.g. the European Union Technical Guidance Document (European Commission, 2003), are very comprehensive and have been developed for assessing single chemicals. Risk assessments are only available for a few of the chemicals used to make plastics. This thesis mainly comprises the hazard identification step and parts of the hazard characterisation step.

1.9. Aim of the thesis

The overall aim of this thesis was to study the environmental and health hazards of chemicals in plastic polymers and products from a toxicological perspective. This was achieved by evaluations of toxicity by standardised ecotoxicity tests and by identifying the hazards of chemicals used to produce different plastic polymers.

The specific objectives were to:

- determine the acute toxicity of substances leaching from a variety of plastic products [I-II], synthetic textiles [III], and discarded electronic products [IV],
- compare toxicity for different plastic polymer types, product types and components [I-IV],
- identify which class of toxicants that was causing the toxicity [I-IV],

- compile and identify the environmental and health hazards of chemicals used in plastic polymer production [V],
- make a hazard ranking of the polymers based on monomer classifications [V],
- make initial hazard assessments of the polymers [V],
- identify hazardous substances used in polymer production for which evaluation of risks are needed [V].

2. Methods and approach

The methods used are described in detail in the different papers, but are summarized and discussed here.

2.1. Determination of plastic product leachate toxicity

Since there is such a diversity in the chemical composition of plastic products and basically no knowledge on toxicity of leachates from plastic products, a screening approach with leaching tests, bioassays and toxicity characterisations was chosen. In total 83 plastic products and synthetic textiles were tested. In addition, 68 metal, mixed material or plastic components from discarded electronic products were tested.

2.1.1. Product leaching tests

In order to screen many different products, short term leaching tests were chosen. All products were leached in deionised water during a short term period (1 or 3 days). By using deionised water the comparability is increased and the leachate can be used directly for toxicity testing on any aquatic test species, after the addition of the specific stock solutions required by the test organism. Distilled water is also the required test medium in the EU for testing migration from plastic materials into aqueous food (European Council, 1982). The pH of the deionised water was 7.0, which could represent the pH of a lake or river (neither acidic, nor alkaline).

There is no general standardised method for testing leaching of plastic products for subsequent toxicity testing. The available methods have been developed for measuring migration levels of chemicals from plastic material and articles that are in contact with food into food simulants (e.g. EN 1186-14:2002), or for measuring migration into artificial sweat or saliva.

Two main methods for leaching were used, one batch leaching method based on CEN (2002) for the characterization of wastes, and one diffusion leaching method. One drawback with the batch leaching method, which involves shaking, is that most VOCs are probably not included in the leachate (Bjerre Hansen and Andersen, 2006). This probable VOC loss may be less with the diffusion leaching method, but can still be considerable (e.g. during preparation of concentration series). Both methods show the test-specific release of contaminants and not the potentially leachable fraction or total amount (Bjerre Hansen and Andersen, 2006) as extraction tests do.

The leaching temperature was either room temperature (≈20°C) [I, IV] or 50°C [II, III]. A higher temperature was used in two of the studies because it was assumed that it could increase leaching, which had been shown in several leaching studies, and because it is a realistic temperature that the surface of a plastic material may reach when exposed to sunlight outdoors. A dark plastic material may be as much as 60°C warmer than the surrounding air, and a comparison between black and white PVC foils showed a 15-23°C higher surface temperature for the black foils (Wypych, 1999). A higher temperature may, however, increase the release of dissolved gases (Tölgyessy et al., 1993), for instance volatile organic compounds. The reasons for increasing the leaching period from 24 h [I, IV] to 3 days [II, III] was partly because it was convenient; leaching can be initiated on Friday, and toxicity testing (screening, EC50 determination and TIE) can be performed Monday to Friday; and partly to compensate for the possible slower leaching when switching from shaking to leaching by diffusion.

Most products were cut into smaller pieces to enable testing of products with irregular shape and to increase the exposed surface area, which may enhance leaching. Glass laboratory materials were used during leaching and toxicity testing to avoid absorption of hydrophobic substances onto plastic laboratory ware (Figure 2).

Figure 2. Plastic product (bib for babies) [I] (left), and synthetic textiles (sporting sweater, stretch pants, and knitted muffler) [III] (right), prior to leaching.

The highest leaching concentrations for the plastic materials were either 100 or 250 g plastic/L (corresponding to a liquid to solid (L/S) ratio of 10 and 4, respectively), and were lower for the mixed material fraction (50 g/L) and metal fraction (25 g/L) of the electronic products. All products were removed prior to toxicity tests.

2.1.2. Toxicity tests with *Daphnia magna*

The test species used was the cladoceran *Daphnia magna* (water flee), a small zooplanktonic crustacean, which is pelagic, filter feeding, and a primary consumer in small freshwater habitats (Figure 3). *Daphnia magna* has been extensively used since the mid 1970s in regulatory testing and ecotoxicological research (Koivisto, 1995). For instance, in REACH *Daphnia* is specified as the preferred invertebrate for short-term toxicity testing, which is a standard information requirement for substances manufactured or imported in quantities >1 ton (European Parliament and Council, 2006). The relatively small size, short life span, high fecundity, ability of asexual reproduction, and ease to culture in the laboratory, makes it suitable for toxicity testing (Koivisto, 1995). *Daphnia magna* is also considered to be a sensitive organism, in general more sensitive to metals and other contaminants than fish (Jonczyk and Gilron, 2005). Some, e.g. Koivisto (1995), argue that *Daphnia magna* is not ecologically representative because it differs too much from other freshwater zooplankton, in terms of its larger size, different habitat, life history (more and smaller neonates that mature later), and poor ability to withstand fish predation.

Daphnia magna was chosen because it was considered to be a suitable test organism for screening studies; standardised reliable test methods were available; it is a sensitive species; the use of larger test organisms and vertebrates could be avoided; and there was a steady culture available at the laboratory. Acute toxicity tests (with immobility as toxic endpoint) were chosen partly to be able to screen many products, and partly because the variety in products, as well as the largely unknown chemical composition, made it difficult to know which chemicals that could be released and which toxic effect(s) to anticipate. However, acute toxicity is not the most probable toxic response to anticipate from plastic product water lechates (further discussed under 3.1.3).

Standardised toxicity tests according to ISO (1996) were chosen to increase comparability. The standard requires that stock solutions are added to give a hardness of 250 mg $CaCO_3$/L and a pH of 8. This is considered as a very hard water (>150 mg $CaCO_3$/L), but is well within the wide range of hardness of world ground waters (0->1000 mg $CaCO_3$/L), which primarily depends on the type of underlying bedrock (Hiscock, 2005). The pH of the leachate during the toxicity test could represent the pH in sea water, which has an average around pH 8 (Garrison, 2007). Both hardness of the water and pH can have a great influence on toxicity and are important to take into account when assessing the risks in a certain ecosystem. For instance for many metals, metal toxicity is decreased by increasing hardness (because of complexation, and competition of binding sites on the organism, e.g. the gill surface), and metal release is increased by a lower pH (Manson, 2002).

Figure 3. Test organism *Daphnia magna* (size: 0.8 mm newborn, 5-6 mm adult), and Petri dishes during toxicity tests.

2.1.3. Toxicity Identification Evaluations (TIEs)

The chemical composition of a leachate from a plastic product, textile, or electronic product is to a great extent not known. In a screening approach when many different products and possible substances are involved, it is very difficult to choose the right chemical analyses. It is comparably easy to analyse for metals, but when organic substances are involved it is necessary to know which substances to analyse for. Even then, these analyses are time consuming and expensive without being extensive. By using Toxicity Identification Evaluations, phase I, based on US EPA methods (1991) to characterise classes of toxicants the number of possible toxicants is narrowed down, and information on which classes of toxicants (e.g. metals or hydrophobic organics) that are causing the toxicity can be obtained. Complete TIEs also include identification (phase II) and confirmation (phase III), in which also chemical analysis are included (Norberg-King et al., 2005). These can give information of which chemical substance that is causing the toxicity.

In this study only initial phase I TIEs were used. The number of different manipulations of the toxic leachate was usually limited to two or three. C18 solid phase extraction was used to remove hydrophobic organics, CM solid phase extraction was used to remove cations, and EDTA and sodium thiosulfate addition were used to complex cationic metals. Subsequent toxicity tests were performed to compare toxicity in manipulated and non-manipulated leachates.

2.2. Hazard ranking and assessment of plastic polymers

Also in the hazard ranking of plastic polymers a wide approach was chosen, with the intention to cover a large number of both thermoplastic and thermosetting polymers. A hazard ranking of plastic polymers was made based on monomer composition and environmental and health hazard classifications.

2.2.1. Chemicals in plastic polymer production and hazard classifications

Data on which chemical substances that were needed to produce the different plastic polymers were collected from the polymer literature (compiled in Report S1: supplementary material to paper V). For all substances which were identified as used in the production of each polymer type, hazard classification data were collected, mainly from the EU classification, labelling and packaging (CLP) regulation (European Parliament and Council, 2008) including the 1st Adaptation to Technical Progress (European Commission, 2009). All these substances and classifications are presented in Table S1 (supplementary material to paper V) in the very back of this thesis.

2.2.2. Hazard ranking model

There are several ranking and scoring systems for chemicals (evaluated by Davis et al., 1994), but there is no consensus on which of the methods that is the most effective. A new hazard ranking method based on hazard classifications was developed for this study. The EU classification, labelling and packaging (CLP) regulation was chosen because it contains harmonised classifications, and is based on the UN Globally Harmonized System (GHS) (European Parliament and Council, 2008; UN, 2009). Therefore, the model and the data in the model can be regarded as having an almost global validation. No previous ranking method was available for the GHS or CLP.

In the ranking model the CLP hazard classes for environment and health hazards, with accompanying categories, were sorted into five levels of hazards (*I-V*). The hazard classes and categories sorted as level *V* were: carcinogenicity, mutagenicity and reproductive toxicity (categories 1A & B), and hazardous for the ozone layer. Those sorted as level *IV* were: mutagenicity (cat. 2), acute toxicity (cat. 1 & 2), respiratory/skin sensitisation, specific target organ toxicity – single/repeated exposure, and hazardous to the aquatic environment (chronic cat. 1 & 4). Each level was assigned a rough hazard grade, increasing with a factor of 10 for each level of hazard (*I-V*). The hazard grades for each classification that a substance has were summarised to create a hazard score for the substance.

In the ranking of the polymers only the basic building blocks that define the polymer, i.e. the monomers (with a few exceptions), were included. These can not be changed without changing the polymer. Other chemicals needed for polymerisation to occur, such as catalysts, solvents, etc., were not included because they would add to much variability to the ranking. These substances have, however, been presented and discussed separately. Additives that are compounded with the polymer to make different plastic products were excluded because of the extreme diversity and variability.

The hazard score for the substance (in this case the monomer) was multiplied with the weight fraction of the monomer in the polymer. Finally the sum of the hazard scores for all monomers included in the polymer type was calculated and a hazard ranking of the different plastic polymers was made.

The hazard ranking model works well for separating the different levels of hazards, but is rough both in terms of hazard levels and hazard grades, and could need some refinement. The hazard scores should, therefore, not be regarded as absolutely true figures but rather as a way to enable an approximate relative ranking, and to identify presence of hazardous substances. A valuable contribution to the Globally Harmonised System would be the development of a harmonised grade for each hazard classification. These grades could be used to facilitate comparisons between different substances and could be used in hazard and risk assessments when many substances are involved.

2.2.3. Initial assessments

The assessments made for the different polymers do not cover the strict definition of hazard assessments (described in 1.8) and are, therefore, called initial assessments. These mainly comprise assessments of non-classified substances based on 1) available information from OECD SIDS Initial Assessment Reports of substances, 2) assessments of other hazardous substances used than monomers, and 3) comparisons between hazard rank and global annual production. Global annual production was used as a rough measure for quantifying the hazard in order to identify which polymers should be prioritised for further risk assessments.

Exposure and effect assessment have been discussed but were not possible to include in this study. Even when dealing with single chemicals, such assessments can be a hard challenge, although easy compared to assessing complex products such as plastic products.

3. Results and discussion

In this chapter the results from papers [I-V] are summarized and discussed.

3.1. Acute toxicity from product leachates

Acute toxicity was seen in all toxicity studies [I-IV] in approximately 30% of the samples.

3.1.1 Toxicity of plastic products and synthetic textiles

Twenty-eight of the leachates from the 83 studied plastic products and synthetic textiles [I-III] showed acute toxicity to *Daphnia magna* (Table 1). This represents 33.7% of the tested products. Since the highest test concentration was lower (100 g/L) for the products in paper I, the results can also be expressed as 22 of the 83 tested (i.e. 26.5%) had 48-h EC50 ranging between 1 and ≈100 g/L. The toxic products from paper I are shown in Figure 4.

Table 1. The 28 toxic plastic product [I, II] and synthetic textile [III] leachates and their 48-h EC50s for *Daphnia magna* (modified from papers I-III).

Product	**Plastic type**	**48 h EC50s g plastic/L**		**TIE indication of toxicant**	**Leaching test**
		Repl 1	**Repl 2**		
Plastic products					
I. Artificial leather, brand S	Plasticised PVC	8	8	organics (& metals)	24 h shaking 22°C
I. Artificial leather, brand,G	Polyurethane	38	31		24 h shaking 22°C
I. Artificial leather, brand M	Plasticised PVC	26	22	organics (& metals)	24 h shaking 22°C
I. Floor	Platicised PVC with polyurethane surface	54	50		24 h shaking 22°C
I. Children's handbag	Polyurethane	44	54		24 h shaking 22°C
I. Bath tub squirt toys	Plasticised PVC	≈ 100	59		24 h shaking 22°C
I. Inflatable bathing ring	Plasticised PVC	71	75		24 h shaking 22°C
I. Table cloth	Plasticised PVC	62	76		24 h shaking 22°C
II. Watering can	High-density-polyethylene	17	24		3 d diffusion 50°C
II. Laboratory gloves	Plasticised PVC	2	4	metals	3 d diffusion 50°C
II. Boat fender	Plasticised PVC	21	11	organics	3 d diffusion 50°C
II. Arm pads for floating	Plasticised PVC	79	70	organics	3 d diffusion 50°C
II. Rain poncho	Plasticised PVC	172	160	organics (& metals?)	3 d diffusion 50°C
II. Wet room wall carpet	Plasticised PVC	235	219		3 d diffusion 50°C
II. Super epoxy (filler)[a]	Epoxy (cured)	10	2	organics	3 d diffusion 50°C
II. Marine epoxy (filler)[a]	Epoxy (cured)	9	6	organics	3 d diffusion 50°C
II. Quick epoxy glue[a]	Epoxy (cured)	44	39		3 d diffusion 50°C
II. Laminating epoxy[a]	Epoxy (cured)	>80	27		3 d diffusion 50°C
II. Epoxy putty (sealant)[a]	Epoxy (cured)	114	99		3 d diffusion 50°C
Synthetic textiles					
III. Awning cloth[b]	Polyacrylonitrile (acrylic) impregnated with polytetrafluorethylene (PTFE; Teflon®)	1	1	organics	3 d diffusion 50°C
III. Furniture fabric	Polypropylene	4	3		3 d diffusion 50°C
III. Mesh fabric[b]	Plasticised PVC coated polyester (PET)	7	8	organics	3 d diffusion 50°C
III. Baby diaper outer material[c]	Polypropylene and polyethylene	75	68		24 h shaking 22°C
III. Knitted muffler	Polyacrylonitrile (acrylic)	108	131		3 d diffusion 50°C
III. Furniture fabric	Polyacrylonitrile (acrylic; 73%), polyester (27%)	176	185		3 d diffusion 50°C
III. Curtain	Polyamide (nylon)	172	145		3 d diffusion 50°C
III. Wool imitation fabric	Polyacrylonitrile (acrylic)	124	180		3 d diffusion 50°C
III. Stretch pants (golden)	Polyester (92%), thermoplastic polyurethane (elastane; 8%)	210	201		3 d diffusion 50°C

[a] Cured epoxy resin
[b] Technical fabric
[c] The non-woven material was tested, excluding the absorbing core and covering top sheet. Some unspecified elastic material was also present.

The applications for the products varied, and no specific product category was tested. Examples of product categories include drinking water and ground pipes, floors, fillers, mattress, household articles (e.g. food and water containers, table cloths, plates), articles intended for small children (toys, floating aid and diapers), garbage bag, rain and skin protection, and synthetic textiles (e.g. clothes and furniture and technical fabrics). The sample size for the different product categories is not large enough to draw general conclusions for respective product category. However, a few patterns have been noted. Considerably many leachates from products intended for children (5/13) were toxic. These include a floating ring, arm pads for floating, children's handbag, a bath tub squirt toy, and a diaper (excluding the absorbing core and top sheet). None of the 12 leachates from articles for food or drinking water contact were acutely toxic, an outcome which was expected since there are regulations for food contact materials (mentioned in 1.3). Among the synthetic textiles technical fabrics and furniture fabrics were among the most toxic ones, and the fabrics in the clothes category were less toxic.

Figure 4. Plastic products (from paper I) which caused toxic leachates, i.e.: artificial leathers (brand S, G and M), children's handbag, bath tub squirt toys, floor material, table cloth (transparent), and inflatable bathing ring. The CD was only toxic when cut into pieces and the silver layer was exposed [I].

Also the distribution of polymer types is uneven among the products, and the sample sizes are too small draw conclusions valid for the polymer type. However, a few patterns can be seen, most evident for PVC and epoxy. The number of toxic samples per polymer type is presented in Table 2. Leachates causing acute toxicity were produced by all epoxy products (5/5), almost all (11/13) plasticised PVC products, three out of four soft polyurethane products (including those mixed), four out of six polyacrylonitrile fabrics (including those mixed), and only one each of the 13 polyethylene, 10 polyester and 9 polypropylene products. The two rigid PVC products were not toxic. The toxic products were either soft to semi-soft plastic products (mainly made of plasticised PVC, and a few made of polyurethane), or epoxy products, or textile products. One exception was a high-density polyethylene watering can (Table 1).

Table 2. Distribution of tested polymers types and toxic product leachates.

Plastic polymer	**Toxic leachates/ tested leachates**
Polyethylene (HDPE 1/8; LDPE 0/1; MDPE 0/4)	**1/13**
Polyethylene and/or polypropylene	**1/4**
Polypropylene	**1/9**
Rigid PVC	0/2
Plasticised PVC	**11/13**
Polyurethane/plasticised PVC mix	**1/1**
Polyurethane	**2/3**
Polyester/thermoplastic polyurethane	**1/2**
Polyester	0/8
Polyacrylonitrile/polyester mix	**1/1**
Polyacrylonitrile (acrylics)	**2/4**
Polytetrafluorethylene (PTFE; Teflon)/ polyacrylonitrile mix	**1/1**
Polytetrafluorethylene (PTFE; Teflon)	0/1
Nylon	**1/3**
Nylon/polyurethane mix	0/1
Nylon/polyester mix	0/1
Epoxy	**5/5**
Acrylonitrile-butadiene-styrene	0/6
Polystyrene	0/2
Polycarbonate	0/1
Polymethyl methacrylate	0/1
Melamine-formaldehyde	0/1

In bold: polymer types with toxic leachates.

Release of non-polymeric substances is expected to be larger for more rubbery (soft) polymers, e.g. the plasticised PVC and soft polyurethane products, because they have larger gaps between the polymer molecules, compared to crystalline polymers which have a greater degree of molecular packing (Brydson, 1999; Godwin and Krauskopf, 2008). Plasticised PVC also contains larger amounts of additives which may be available for leaching. For instance plasticisers can be used in amounts up to 60 percentages by weight, but most commonly 35-40 weight percent is used (Navarro et al., 2010). For the epoxy products uncured residuals from resin and/or hardener are likely to have caused the observed toxicity. Polyacrylonitrile and polyacrylonitrile mix fabrics were overrepresented among the toxic textile leachates. However, a valid comparison between plastic fibre types could not be made because the sample size was too small, the distribution between fibre types was uneven, mixed fabrics were involved, and the toxicants were not identified and could, therefore, have been any textile processing chemical.

The initial Toxicity Identification Evaluations (TIE) made on the most toxic leachates indicated that hydrophobic (non-polar) organics were the major cause of toxicity for nine of the ten tested leachates, and that cationic metals may have been responsible for some of the toxicity in several of the samples (Table 1). For the laboratory gloves the TIE indicated that cationic metals were the major cause of toxicity, and metal release was also confirmed by chemical analysis [II].

3.1.2. Toxicity of discarded electronic products

Among the discarded electronic products 18 of the 68 leachates showed acute toxicity to *Daphnia magna* [IV]. This represents 26.5%, which is less than for the plastic products and synthetic textiles [I-III]. These results are, however, not comparable because the highest test concentrations for the tested electronic product were much lower for metal parts (25 g/L) and the mixed material parts (50 g/L), than for the plastic product and synthetic textiles (100-250 g/L). If instead only the 48-h EC50 values ≤25 g/L are considered, a higher share of low EC50s (i.e. more toxic) were found among electronic products, than among the plastic and textile products. However, the test set-up was slightly different, and besides, studies like these should primarily be used for comparing a more similar category of products.

The eight most toxic leachates had 48-h EC50s ranging from 0.4 to 20 g/L and belonged to the metal or the mixed material category (Table 3). All five tested electronic products contained components that generated at least one toxic leachate. The TIE indicated that cationic metals were the major cause of toxicity for the majority of the leachates, and that hydrophobic organics may have been involved to a lesser extent in a couple of the leachates.

Table 3 The eight most toxic leachates from discarded electronic product components made of metals and mixed materials respectively and *Daphnia magna* 48-h EC50s (modified from paper IV).

Sample	**Component(s)**	**Type of electronic product**	**48 h EC50 g/L**		**TIE indication of toxicant**
			Repl 1	**Repl 2**	
30 metal	IDE cable clips	Computer	5.4	5.7	metals
31 metal	Metal studs	Computer	4.4	7.9	metals
4 mixed mat.	Circuit sheet	Keyboard	0.9	0.4	-
37 mixed mat.	Circuit sheet	Keyboard	2.3	2.7	cations
14 mixed mat.	Circuit board	Computer mouse	6.6	7.8	metals, (organics?)
10 mixed mat.	Cord	Phone modem	18	13	
18 mixed mat.	Mixed parts (screen frame, microphone, speaker, antenna)	Cell phone	15	18	metals
1 mixed mat.	Circuit board	Keyboard	13	20	metals

Leaching was performed by diffusion for 3 d at 23°C.

None of the tested 13 plastic components showed any toxicity at the highest test concentration (100 g/L). Possible explanations for lack of toxicity could be that hard plastics are not particularly acutely toxic under the existing test conditions [I-II]; that possible content of readily available non-polymeric substances, which are the most likely to leach under the specific test conditions, had already been released during the use phase or were not released in high enough concentrations; and that most plastic pieces were covers and casings which had to be cleaned with a damp cloth to remove dirt prior to leaching, and this may also have removed some possible surface contaminants. In other studies plastic fractions from electronic products have been shown to release brominated flame retardants mainly to methanol (20%), and to a lesser extent to distilled water (Kim et al., 2006). The plastic fraction can also be contaminated with heavy metals. For instance, Morf et al. (2007) found average concentrations >1000 mg/kg for Cu, Sb, Sn, Zn, Pb, and Ni in the plastic fraction of various electronic products.

3.1.3. Acute toxicity and other toxic effects

The laboratory studies in papers I-IV show the acute toxicity of product leachates. This type of toxicity requires exposure to high concentrations of toxicants, or exposure to very acutely toxic toxicants, in order for the adverse effect (e.g. immobility, death) to occur. This means that large amounts of toxicants or very toxic chemicals had to leach from the materials under the short leaching period (1-3 days) in deionised water. For many plastic products leaching of chemical substances from the plastic materials is more likely to occur at low concentrations under a prolonged time period, and in many cases also under the influence of degradation. This statement is based on: a) the available data of chemical release from plastic products (examples given under 1.5) which are usually measured in the lower concentrations ranges, and b) on the physical structure of the polymer in which the gaps between polymer molecules are often quite small and, thereby, decreases the migration potential. Many other toxic effects such as carcinogenicity, mutagenicity, reproductive toxicity, sensitisation and chronic aquatic toxicity, as well as endocrine disruption, are not detected in the acute toxicity tests, but are common for many of the chemicals used for producing plastic polymers, as shown in paper V. However, acute toxicity tests can be used for screening purposes to identify toxic products, but should not be used alone to conclude that a certain plastic product is non-toxic.

3.2. Hazard ranking and initial assessments

In this section only some of the results from paper V are presented and the reader is referred to this paper for further information. The plastic polymers that ranked as the most hazardous ones are made of monomers that are classified as mutagenic and/or carcinogenic (category 1A or 1B). These polymers belong to the polymer families of polyurethanes, polyacrylonitriles, PVC, epoxy resins, and styrenic copolymers (ABS, SAN and HIPS). All have a large global annual production, ranging between 1 and 37 million tons. PVC has the largest production of them, accounting for 17% (by weight) of the world plastic demand (PlasticsEurope MRG, 2008). All these highly ranked polymers should be prioritised for assessments of risks.

A considerable number of polymers (31 out of 55) are made of monomers that have hazard classifications belonging to the two highest (i.e. levels *IV-V*) of the five hazard levels in the ranking model. These polymers are presented in Table 4. The polymers which are made of level *IV* monomers and, in addition, have a large global annual production (1-5 million tons) are phenol formaldehyde resins, unsaturated polyesters, polycarbonate, polymethyl methacrylate, and urea-formaldehyde resins.

Table 4. Hazard ranked plastic polymers that are composed of monomers with hazard classifications that belong to hazard levels *IV* or *V* (modified from paper V).

Rank	Hazard score	Polymer	Monomers (weight%)
1	13844	Polyurethane (PUR) [a], polyether based flexible foam, example	**Propylene oxide** (58); **Toluene-diisocyanate** (29); **Ethylene oxide** (7); HCF-134a (6)*
2	12379	Polyacrylonitrile (PAN) with comonomer, example acrylamide	**Acrylonitrile** (92); **Acrylamide** (8)
3	11521	Polyacrylonitrile (PAN)	**Acrylonitrile** (100)
4	10599	Polyacrylonitrile (PAN) with comonomer, example vinyl acetate	**Acrylonitrile** (92); Vinyl acetate (8)
5	10551	Polyvinyl chloride (PVC), plasticized, example with most toxic plasticiser	**Vinyl chloride** (50); **Plasticiser: Benzyl butyl phthalate (BBP)** (50)
6	10001	Polyvinyl chloride (PVC), rigid	**Vinyl chloride** (100)
7*	7384*	Polyurethane (PUR)[a], polyether based rigid foam, example	**Propylene oxide** (31); **4,4'-methylenediphenyl diisocyanate (MDI)** (52); Sorbitol (13)*; Cyclopentane (4)
8	7139	Epoxy resin DGEBPA [a], low mw (450), example with most toxic curing agent	**Bisphenol A** (45); **Epichlorohydrin** (37); **4,4'-methylenedianiline (MDA)** (18)
9	6957	Modacrylic, example with vinylidene chloride	**Acrylonitrile** (60); Vinylidene chloride (40)
10	6552	Acrylonitrile-butadiene-styrene (ABS) terpolymer	Styrene (58); **Acrylonitrile** (22); **1,3-butadiene** (20)
11*	5001*	Polyvinyl chloride (PVC), 50% non-classified plasticiser	**Vinyl chloride** (50); Diisodecyl phthalate DIDP (50)*
12	4515	Epoxy resin DGEBPA[a], low mw (450), example with least toxic curing agent	**Bisphenol A** (43); **Epichlorohydrin** (35); 4,4'-diamino diphenyl sulfone (DDS) (22)
13	4226	Epoxy resin DGEBPA[a], high mw (3750), example with non-classified curing agent	**Bisphenol A** (67); **Epichlorohydrin** (30); Dicyandiamide (3)
14	2788	Styrene-acrylonitrile (SAN) copolymer	Styrene (76); **Acrylonitrile** (24)
15	1628	High-impact polystyrene (HIPS)	Styrene (92); **1,3-butadiene** (8)
16	1500	Polyoxymethylene (POM), homopolymer	**Formaldehyde** (100)
16	1500	Phenol formaldehyde resins (PF) [a], example resol	**Phenol** (61); **Formaldehyde** (39)
17	1450	Phenol formaldehyde resins (PF) [a], example novolacs	**Phenol** (72); **Formaldehyde** (18); **Hexamethylenetetramine** (10)
18*	1414*	Unsaturated polyester [a] (UP), example with methyl metacrylate	**Phthalic anhydride** (31); **Methyl methacrylate** (30?); Propylene glycol (18)*; **Maleic anhydride** (21)
19**	1187**	Poly(m-phenyleneisophtalamide) (MPD-I) (Nomex®)	Isophthaloyl chloride (65)**; **m-phenylenediamine** (35)
19	1177	Polycarbonate (PC), example with phosgene	**Bisphenol A** (70?); **Phosgene** (30?)
20*	1117*	Unsaturated polyester [a] (UP), example with styrene	**Phthalic anhydride** (31); Styrene (30); **Maleic anhydride** (21); Propylene glycol (18)*
21**	1094**	Thermoplastic polyurethanes (TPU) polyester based rigid example	Adipic acid, Ethylene glycol & 1,4-Butanediol** (35); **4,4'-methylenediphenyl diisocyanate (MDI)** (49); 1,4-Butanediol (16)*
22	1021	Polymethyl methacrylate (PMMA)	**Methyl methacrylate** (100)
23	897	Polyphenylene sulfide (PPS)	**1,4-dichlorobenzene** (65); Sodium sulphide (35)
24*	882*	Melamine-formaldehyde resin (MF) [a]	**Formaldehyde** (59); Melamine (41)*
25	871	Polyoxymethylene (POM) copolymer, example with ethylene oxide	Trioxymethylene (96); **Ethylene oxide** (4)
26**	829**	Poly(p-phenyleneterephtalamide) (PPD-T) (Kevlar®)	Terephthaloyl chloride (66)**; **p-phenylenediamine** (34)
27*	750*	Urea-formaldehyde resin (UF) [a]	**Formaldehyde** (50); Urea (50)*
28**	610**	Polycarbonate (PC), example with diphenyl carbonate	**Bisphenol A** (50); Diphenyl carbonate (50)**
29**	556**	Thermoplastic polyurethanes (TPU) polyester based glycol soft example	Adipic acid, Ethylene glycol & 1,4-Butanediol (70); **4,4'-methylenediphenyl diisocyanate (MDI)** (24); 1,4-Butanediol (6)**

[a] Thermosetting plastics

In bold: monomers with level *IV* and/or level *V* hazard classifications. These are presented in Table 5.

*Contains ≥10 wt% non-classified substance, but with indication of low level of hazard according to SIDS initial assessment reports.

**Contains ≥10 wt% non-classified substance, for which ranking may be underestimated, due to elevated concern according to SIDS initial assessment reports, or lack of data.

The most frequent hazard classifications among the monomers in the 55 polymers were: skin sensitization 1, respiratory irritation 1, acute toxicity 3 (inhaled; skin; oral, respectively), serious eye irritation 2, carcinogenic 1A & 1B, and skin corrosion 1A & 1B. Environmental hazard classifications were less frequent for the monomers than health hazard classifications. The monomers which have hazard classifications that at least belong to hazard level *IV* are presented in Table 5.

Table 5. Monomers from Table 4 that have hazard classifications, which at least belong to hazard level *IV*. Classifications belonging to hazard levels *I-II* are not shown (modified from paper V).

Level IV and V monomers	Hazard classifications and category code (hazard levels III-V)	Hazard score
1,3-butadiene	**Carcinogenicity 1A (V)**, **Mutagenicity 1B (V)**	20001
1,4-dichlorobenzene	**Aquatic chronic 1 (IV)**, Carcinogenicity 2 (III), Aquatic acute 1 (III)	1210
4,4'-methylenedianiline (MDA)	**Carcinogenicity 1B (V)**, **Mutagenicity 2 (IV)**, **Skin sensitization 1 (IV)**, **Specific target organ toxicity -single exposure 1 (IV)**, Specific target organ toxicity - repeated exposure 2 (III), Aquatic chronic 2 (III)	13200
4,4'-methylenediphenyl diisocyanate (MDI)	**Respiratory sensitization 1 (IV), Skin sensitization 1 (IV),** Carcinogenicity. 2 (III), Specific target organ toxicity - repeated exposure 2 (III)	2240
Acrylamide	**Carcinogenicity 1B (V), Mutagenicity 1B (V),** Specific target organ toxicity - repeated exposure 1 (IV), Reproductive toxicity 2^{f} (III), Acute toxicity 3^{o} (III)	22240
Acrylonitrile	**Carcinogenicity 1B (V)**, **Skin Sensitization 1 (IV)**, Acute toxicity 3^{o,d,i} (III), Serious eye damage 1 (III), Aquatic chronic 2 (III)	11521
Benzyl butyl phthalate (BBP) (Note: plasticiser)	**Reproductive toxicity 1B^{FD} (V)**, **Aquatic chronic 1 (IV),** Aquatic acute 1 (III)	11100
Bisphenol A	**Skin sensitization 1 (IV)**, Reproductive toxicity 2^{f} (III), Serious eye damage 1 (III)	1210
Epichlorohydrin	**Carcinogenicity 1B (V)**, **Skin sensitization 1 (IV)**, Skin corrosion 1B (III), Acute toxicity 3^{o,d,i} (III)	11400
Ethylene oxide	**Carcinogenicity 1B (V)**, **Mutagenicity 1B (V)**, Acute toxicity 3^{i} (III)	20131
Formaldehyde	**Skin sensitization 1 (IV)**, Carcinogenicity 2 (III), Acute toxicity 3^{o,d,i} (III), Skin corrosion 1B (III)	1500
Hexamethylenetetramine	**Skin sensitization 1 (IV)**	1000
Maleic anhydride	**Respiratory sensitization 1 (IV), Skin sensitization 1 (IV)**, Skin corrosion 1B (III)	2110
Methyl methacrylate	**Skin sensitization 1 (IV)**	1021
m-phenylenediamine	**Mutagenicity 2 (IV)**, **Skin sensitization 1 (IV)**, **Aquatic chronic 1 (IV)**, Aquatic acute 1 (III), Acute toxicity 3^{o,d,i} (III)	3410
Phenol	**Mutagenicity 2 (IV)**, Acute toxicity 3^{o,d,i} (III), Specific target organ toxicity - repeated exposure 2 (III), Skin corrosion 1B (III)	1500
Phosgene	**Acute toxicity 2^{i} (IV)**, Skin corrosion 1B (III)	1100
p-phenylenediamine	**Aquatic chronic 1 (IV)**, **Skin sensitization 1 (IV)**, Aquatic acute 1 (III), Acute toxicity 3^{o,d,i} (III)	2410
Propylene oxide	**Carcinogenicity 1B (V)**, **Mutagenicity 1B (V)**	20061
Toluene-diisocyanate (TDI)	**Acute toxicity 2^{i} (IV)**, **Respiratory sensitization 1 (IV)**, Carcinogenicity 2 (III)	3140
Vinyl chloride	**Carcinogenicity 1A (V)**	10001

^{o,d,i}toxic by **o**ral, **d**ermal and **i**nhalation route
^{FD}may damage **f**ertility and the unborn child (**d**evelopment)
^{f}suspected of damaging **f**ertility
In bold: level *IV* and *V* classifications

Several solvents used during polymerisation are classified as carcinogenic and mutagenic, or toxic for reproduction (category 1A & 1B), or very toxic to aquatic life with long lasting effects (aquatic chronic 1), and the most hazardous catalysts are classified as aquatic chronic 1 (see paper V).

Polyethylenes and polypropylene, which alone account for 54% of the world production of plastics (PlasticsEurope MRG, 2008), ranked as least hazardous, as did polyvinyl acetate and ethylene vinyl acetate. Also polyethylene terephthalate (PET), which also have a considerable global annual production, ranked as not particularly hazardous. The monomers used to produce PET were not classified so there is some uncertainty, however, the SIDS Initial assessment reports indicated low level of concern.

Since there is neither a hazard class in the GHS, nor hazard classifications in the CLP for endocrine disrupters, they could not be included in the ranking model. A few of the monomers used in plastics are under evaluation for endocrine disrupting properties within the European Union strategy for endocrine disrupters (European Commission, 2008). These include bisphenol A (used in polycarbonate and the main epoxy resin DGEBPA; diglycidylether of bisphenol A), styrene (used in polystyrene and polystyrene copolymers), epichlorohydrin (used in the main epoxy resin DGEBPA) and some phthalates (used in PVC) (Groshart and Okkerman, 2000; Okkerman and van der Putte, 2002). They have preliminary been assigned category 1 based on evidence of human effects, and assigned high level of concern due to risk of high exposure (Groshart and Okkerman, 2000; Okkerman and van der Putte, 2002). The polymers containing these monomers could be ranked as more hazardous if endocrine disruption is identified.

Another factor that can affect the ranking is a subsequent assessment of the environmental fate of the monomers in the hazardous ranked polymers. For instance, if the monomer is very volatile and/or very rapidly photo-degrading, readily biodegradable, and not bioaccumulating, the hazards may mainly be confined to the production phase with worker exposure through air. This is because many of the monomers and solvents used are volatile.

In paper V hazardous substances used in the production of different plastic polymers were identified. From a general point of view all level *V* substances ought to be considered as candidates for phase out. However, if no alternatives exist, the risks should be evaluated for decisions on either need for risk reduction measures or phase out. For level *IV* substances it is advisable with substitution when less hazardous alternatives exist, and evaluation of the need for risk reduction measures if there are no alternatives.

The hazard ranking model was found to be a useful tool for identify hazardous substances in polymer production and for ranking the polymers, and could be used in other hazard or risk assessments for comparing substances, mixtures or articles. The results from paper V and its supplementary material can be used for further hazard and risk assessment of those plastic polymers identified as hazardous.

3.3. Most hazardous ranked polymers versus toxic products

When comparing the polymers types which were ranked as most hazardous with the leachates from plastic products that were toxic to *Daphnia magna*, there is a correlation. The most hazardously ranked polymers polyurethane, polyacrylonitrile, polyvinyl chloride, and epoxy, were also the polymers used in the products that had the most toxic leachates, with a few exceptions.

Since the ranking is based on monomer composition this would, if this correlation is valid also for a greater number of plastics, mean that residual monomers were leached in such high quantities from these products to cause acute toxicity. For the epoxy products, this correlation is likely to be valid. Uncured resin DGEBPA or its monomers (bisphenol A and epichlorohydrin) and some of the curing agents are the most likely cause of toxicity seen for the epoxy products. For the other polymer types there are several other possible explanations for toxicity. The PVC and polyurethane products were soft to semi-soft, which facilitates migration of chemicals. In the plasticised PVC also the quantities of plasticisers and other non-bound additives, which may be available for leaching, are larger than for other plastic types. The polyacrylonitrile products were synthetic textiles. Any residual monomers in the fibres are according to Smith (2003) likely to be released during textile manufacturing processes, and, besides, there are many other possible chemical residues emanating from the processing of the textile fabric that could cause toxicity. Other reasons that argue against monomers being responsible for most of the toxicity seen in the leachates are that:
a) the residual monomer content is generally quite low in a plastic product and, therefore, possible effects are more likely to be seen in chronic studies, b) many of the hazardous monomers are volatile and may have been lost during the leaching and preparation of solutions for toxicity testing, and c) none of the monomers which the tested plastic products were composed of are classified as very acute toxic to aquatic organisms, i.e. aquatic acute (category 1) (Table 2, paper V).

4. Conclusions

- Substances causing acute toxicity to *Daphnia magna* leached from one third of all 83 tested plastic products and synthetic textiles even during the short term (1-3 d) leaching period in deionised water [I-III].

- The toxic leachates came mainly from products that were soft to semi-soft, i.e. plasticised PVC (11/13) and polyurethane (3/4), and from epoxy products (5/5), and from synthetic textiles made from various plastic fibres [I-III].

- Only one each of the 13 polyethylene, 10 polyester and 9 polypropylene leachates were acutely toxic [I-III].

- A considerable number of leachates from products intended for children (5/13) were toxic [I-III].

- None of the 12 leachates from articles for food or drinking water contact were acutely toxic [I, II].

- The toxic leachates from discarded electronic products came from the mixed material or the metal fraction, but none came from the pure plastic fraction [IV].

- Toxicity Identification Evaluation, performed on some leachates, indicated that the major toxicants were hydrophobic organics for the plastic product [I, II] and synthetic textile [III] leachates, and metals for the electronic product leachates [IV].

- Many other toxic responses than acute toxicity are highly relevant in plastic leachates [V], and leaching is suspected to be more likely to occur at low concentrations during a long period of time.

- The plastic polymers ranked as most hazardous are made of monomers classified as either carcinogenic or both carcinogenic and mutagenic (category 1A or 1B) [V].

- These belong to the polymer families of polyurethanes, polyacrylonitriles, PVC, epoxy resins, and styrenic copolymers (ABS, SAN and HIPS), and have a large global production (1-37 million tons/year). PVC accounts for 17% of the global production of plastics [V].

- The polymers that ranked as least hazardous, i.e. polypropylene and polyethylene, account for 54% of the global production of plastics [V].

- A considerable number of polymers (31 out of 55) are made of monomers that belong to the two highest of the ranking model's hazard levels, i.e. levels *IV* and *V* [V].

- Polymers which are composed of level *IV* monomers, and also have a large global production (1-5 million tons/year), are phenol formaldehyde resins, unsaturated polyesters, polycarbonate, polymethyl methacrylate, and urea-formaldehyde resins [V].

- The most toxic plastic product leachates [I, II, III] were dominated by the polymers which had been ranked as the most hazardous [V], however, in many cases additives were suspected to be a more likely cause of toxicity than monomers.

- For several of the identified hazardous substances used in polymer production the risks ought to be evaluated for decisions on need for risk reduction measures, substitution, or even phase out [V].

- The hazard ranking model is a useful tool for comparing substances, mixtures or articles which can be used in hazard and risk assessment.

- There is a need to assess the risks from exposure in a wider context, including plastic pollution in the environment, degradation products, hazardous additives and mixture toxicity.

5. A more sustainable use of plastics

Considering

- the large global production of plastics and their omnipresence in both society and the environment,
- the persistence and partial degradation of plastic products,
- the large amounts of plastic waste and microplastic pollution in the world oceans,
- plastic diversity by means of types and applications,
- littering, poor waste management and low recycling rates,
- recycling obstacles because of heterogeneity,

as well as

- the use of hazardous chemicals in production, and the potential emissions of hazardous chemicals during the entire lifecycle,

there is a great need to assess the risks associated with plastics.

Exposure and effect assessments are important in order to assess the risks. This can be done by complementing the work in paper V, with predictions of environmental fate for level *V* and level *IV* monomers, and with data on degradation and degradation products of plastic materials under environmental conditions. Long term leaching, which reflects specific exposure scenarios during the use phase and the end of life phase under the influence of degradation, would be valuable, and bioassays studying chronic effects would be desirable. Research on occurrence of plastics in the oceans and the effects of microplastics is ongoing (Bowmer and Kershaw, 2010), and important considering the extensive microplastic pollution. In conclusion, there is too little knowledge of the release of chemicals from plastic products and potential effects.

"In today's world, life without plastics is incomprehensible"(quotation from American Chemistry Council, 2011). That is very true, plastics are extremely necessary in our modern society, but some of the current use and misuse is not sustainable. A more sustainable use of plastics can be achieved by many measures. There is a large potential for reducing the per capita use in the industrialized world, for instance by eliminating excessive packaging material and practicing material reduction when ever possible. By developing more plastics based on bio-based raw materials, the great dependence on non-renewable crude oil and the environmental consequences of crude oil extraction and refining, as well as the contribution to global warming during the end of life phase, can be decreased. Persistence is desired in many applications for long term use, but for short term and single use applications, especially in the packaging sector, the use and further development of biodegradable plastic materials that are fully degradable in the natural environment, are important. Recycling of plastics involve problems since a homogeneous fraction is needed for a similar grade end-product, but the recycling could be facilitated by practicing ecodesign for recyclability and systems for collecting recyclable fractions. Increased recovery (mechanical, chemical or energy recovery) when possible, saves resources and decreases the area needed for landfill. Global action and strong measures to reduce littering are essential to protect our oceans, coastlines, fresh water ecosystems and also our terrestrial environment.

Finally, the diffuse release of chemicals from consumer products (articles), needs to receive more attention. To decrease the hazards and risks from chemicals associated with plastic production and plastic products, reduction measures, substitution, or phase out of the most hazardous chemicals, and maybe even of some polymers (if risk assessments conclude high risk), are important.

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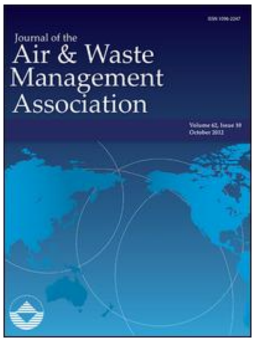

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Compositions of Volatile Organic Compounds Emitted from Melted Virgin and Waste Plastic Pellets

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ABSTRACT

To characterize potential air pollution issues related to recycling facilities of waste plastics, volatile organic compounds (VOCs) emitted from melted virgin and waste plastics pellets were analyzed. In this study, laboratory experiments were performed to melt virgin and waste plastic pellets under various temperatures (150, 200, and 250 °C) and atmospheres (air and nitrogen [N_2]). In the study presented here, low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and the recycled waste plastic pellets were used. The VOCs generated from each plastic pellets were collected by Tenax/Carboxen adsorbent tubes and analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). The result showed the higher temperatures generated larger amounts of total VOCs (TVOCs). The VOCs emitted from the virgin plastic pellets likely originated from polymer degradation. Smaller TVOC emissions were observed in N_2 atmosphere than in air atmosphere. In particular, larger amounts of the oxygenated compounds, which are generally hazardous and malodorous, were detected in air than in N_2. In addition to the compounds originating from polymer degradation, the compounds originating from the plastic additives were also detected from LDPE and PS. Furthermore, various species of VOCs likely originating from contaminant inseparate polyvinyl chloride (PVC), food residues, cleaning agents, degreasers, and so on were detected from the waste plastic. Thus, melting waste plastics, as is conducted in recycling facilities, might generate larger amounts of potentially toxic compounds than producing virgin plastics.

IMPLICATIONS

The issues related to waste plastics have been of serious concern because of limited resources and dump yards for waste materials. Although recycling of waste plastics is a most commonly adapted countermeasure against these problems, it might cause various toxic substances to be released during recycling procedures. In particular, because waste plastics are expected to contain various inseparate contaminants such as PVC, food residues, cleaning agents, degreasers, and so on, production of waste plastics might cause release of larger amounts of potentially harmful VOCs than production of virgin plastics.

INTRODUCTION

In Japan, the issues related to waste plastics have been of serious concern for a prolonged period of time. For instance, dump yards for waste materials are quite limited and expected to be overloaded within next 14.8 yr.[1] In recent years, recycle of waste plastics has become mandated by the Fundamental Law for Establishing a Sound Material-Cycle Society and the Law for the Promotion of Sorted Collection and Recycling of Containers and Packaging, generally known as the Container and Packaging Recycling Law, implemented by the Ministry of the Environment in Japan. Under these laws, waste plastics must be recycled by mechanical procedures, in which melting processes are generally included.

During the melting process, however, volatile organic compounds (VOCs) are likely emitted by thermal degradation of plastic polymers.[2] Because several species of

VOCs emitted from melted plastics are concerned to be toxic, the workers in the mechanical recycling facilities as well as the residents nearby need to be cautious about exposures to those potentially hazardous substances.

To date, various field and/or laboratory studies have been conducted to elucidate the mechanisms of VOC emissions from plastics during melting processes.[3–8] Most of these studies have indicated that the emitted VOCs originated from polymer degradation. However, there might be additional mechanisms responsible for the VOC emissions. For instance, plastic additives such as antioxidants and plasticizer are expected to affect the compositions of emitted VOCs. Furthermore, in the case of recycled waste plastics, residual compounds might affect the VOC emission characteristics. Nevertheless, few studies have been performed to elucidate the mechanisms from these points of view.

The aim of the study reported here is to investigate basic characteristics of the VOC emissions from melted virgin and waste plastics in the molding process for manufacturing recycled products. In particular, we clarified the differences in the VOC emission characteristics from virgin and waste plastics. Virgin plastics, including low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS), were used in the melting experiments. Waste plastic pellets provided by a recycling facility were used for comparison. Dependence of the VOC emission characteristics on temperature and atmosphere was also investigated because the emission characteristics may differ with the surrounding atmospheres under which the melting processes take place.

EXPERIMENTAL METHODS

Plastic Samples

LDPE (NOVATEC injection grade LD802, Japan Polyethylene Corp.), PP (NOVATEC injection grade MA3, Japan Polypropylene Corp.), and PS (GPPS HF77, PS Japan) pellets were used as virgin plastics. Although the manufacturers did not disclose detailed information, it is likely these plastic pellets contained certain amounts of plastic additives because the pellets are designed as raw materials to create final plastic products in the future.

Waste plastic pellets provided by a recycling facility (Kashiwa Ecoplaza) were also used. The waste plastic pellets were reproduced from plastic wastes collected in the city of Kashiwa, Chiba, Japan. The plastic wastes collected in the city were washed and shredded in the recycling facility. Hereafter, metals and polyvinyl chloride (PVC) contained in the wastes were selectively removed by magnetic force and density difference, respectively. The pretreated waste plastics were melted approximately at 150 °C to pelletize the plastics. These pellets were used in this study. According to the recycling facility, the waste plastic pellets consisted mainly of PE, PP, and PS.[9]

Experimental Apparatus

Figure 1 exhibits an experimental apparatus. The sample plastic pellets were placed in a ceramic tubular furnace with an inner diameter of 23 mm (ARF Series, Asahi Rika Corp.). The furnace temperature was controlled with a digital temperature controller (AMF-N, Asahi Rika Corp.). The sample pellets were preheated for 2 min before each experiment. Gas flow rate in the furnace was adjusted at 300 mL/min. The VOCs emitted from the plastic samples were collected in the outflow gas by an automatic thermal desorption tube (ATD; Perkin-Elmer) filled with 100 mg of Tenax TA (Tenax TA 60/80 mesh, Analytical Columns) and 70 mg of Carboxen 1000 (Carboxen 1000 60/80 mesh, SPELCO). The ATD tubes were pretreated at 320 °C for 3 hr in nitrogen (N_2) flow. The air samplings were conducted at 100 mL/min for 10 min by an air pump (Pocket Pump 210-1002, SKC).

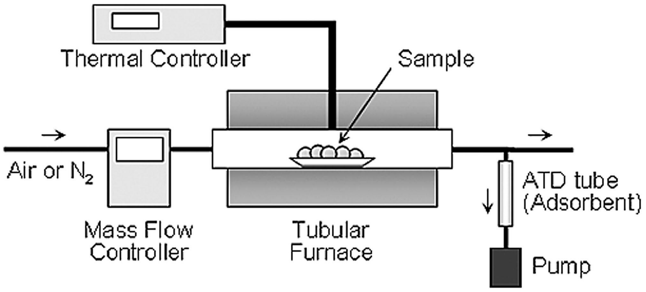

Figure 1. Experimental apparatus.

Experimental Conditions

The VOC emission characteristics were investigated for each temperature and atmosphere. First, to investigate the effect of temperature, 0.3 g of LDPE was heated at 150, 200, and 250 °C in the furnace under air atmosphere, and the VOCs emitted were analyzed. This temperature range was based on the temperature range adopted in recycling facilities. Second, to characterize the differences of the VOC emissions for each kind of plastic, the VOCs emitted from LDPE, PP, PS, and the waste plastic heated at 200 °C were analyzed and compared. To characterize the dependence on atmosphere, these experiments were also performed under both air and N_2 atmospheres.

In these experiments, approximately 0.3 g of plastic pellets were used for each experiment. The 0.3 g of plastic pellets correspond to 12, 14, and 14 pellets for LDPE, PP, and PS, respectively; whereas the numbers of the waste plastic pellets were varied because each waste plastic pellet had different sizes. In this study, triplicate measurements were performed to ensure the reproducibility of each experiment.

Analytical Conditions

The ATD tubes after the samplings were analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). Analytical conditions are shown in Table 1. The VOCs collected by the adsorbents were desorbed by a thermal desorption system (TurboMatrix650, PerkinElmer) and analyzed by gas chromatography (GC; 6890 Series GC System, Agilent) and mass spectrometry (MS; 5973 Network Mass Selective Detector, Agilent).

Data Processing

All of the peaks in the chromatogram were converted to the toluene equivalent amounts. In this study, the lower detection limit was defined based on the peak area of the

Table 1. Analytical condition of GC/MS.

Instrument	Condition
Desorption instrument	TurboMatrix 650
Primary desorption	300 °C, 15 min
Secondary desorption	5 °C (40 °C/min) to 300 °C, 45 min
GC/MS	6890Series GC System, 5973 Network Mass Selective Detector
Column	HP-1 Methyl Siloxane Capillary, 60.0 m × 250 μm × 1.00 μm
Carrier gas	He (1 mL/min)
Column temperature	40 °C, 4 min (7 °C /min) to 280 °C, 10 min
Detection mode	Scan

chromatogram obtained by analyzing the minimum amount of toluene (1 ng) used to plot a calibration curve. The areas smaller than this area were quoted as not detected (ND) (Table 2). The compounds with the matching ratios higher than 70% by a library of Enhanced Chemstation G1701 CA Version C (Agilent) were selected for the subsequent data analysis. Overall, approximately 2600 peaks were selected and analyzed. The selected compounds were classified to each functional group (i.e., aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, etc.) for subsequent data analyses.

RESULTS AND DISCUSSION

Effects of Temperature

Figure 2 shows the amounts of each VOC functional group emitted from LDPE at 150, 200, and 250 °C in air. As shown in the figure, the higher temperature caused higher emissions of VOCs. For instance, the amounts of total VOCs (TVOCs) emitted at 150, 200, and 250 °C were 40 ± 1.2, 121 ± 47, and 902 ± 69 μg/g, respectively. Because polymer degradation is known to proceed more rapidly at higher temperatures,[3,4] the increase of the VOC emissions observed in this study was expected because of the increase of polymer degradation.

Although larger quantities of each VOC functional group were emitted at the higher temperatures, the "other" category showed no distinct difference (Figure 2). Most of the other compounds were identified as butylated hydroxytoluene (BHT), one of the most widely used

Table 2. Amounts of chlorinated HCs, phthalate, and other compounds (in toluene equivalent) emitted exclusively from the waste plastic pellets melted at 200 °C in air and N_2 atmospheres (μg/g).

VOC Emitted	Waste	PP	PS	LDPE
In air				
Chlorinated hydrocarbons				
1,4 or 1,3-Dichlorobenzene	2.35 ± 0.12	ND	ND	ND
1-Chlorododecane	6.62 ± 0.43	ND	ND	ND
Phthalates				
Dimethyl phthalate	2.94 ± 0.67	ND	ND	ND
Diethyl phthalate	2.47 ± 0.65	ND	ND	ND
Other compounds				
2,6-Bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	5.88 ± 1.1	ND	ND	0.540 ± 0.060
Decamethylcyclopentasiloxane	4.42 ± 0.39			
Limonene	0.241 ± 0.051	ND	ND	ND
2-Oxo-3-phenyl-2,3,5,6,7,8-hexahydroindolizine	55.0 ± 4.1	ND	ND	ND
In N_2				
Chlorinated hydrocarbons				
1,1-Dichloroethene	0.460 ± 0.044	ND	ND	ND
1,2,3-Trifluorobenzene	0.0425 ± 0.027	ND	ND	ND
1,4 or 1,3-Dichlorobenzene	2.08 ± 0.40	ND	ND	ND
1,2,4 or 1,3,5-Trichlorobenzene	1.55 ± 1.3	ND	ND	ND
1-Chlorododecane	6.90 ± 0.57	ND	ND	ND
Phthalates				
Dimethyl phthalate	3.14 ± 1.0	ND	ND	ND
Diethyl phthalate	1.90 ± 0.30	ND	ND	ND
Other compounds				
2,6-Di-tert-butylphenol	0.577 ± 0.088	ND	ND	ND
p-Tert-butylbenzoic acid	0.588 ± 0.052	3.35 ± 3.2	ND	ND
2,6-Bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	1.56 ± 0.096	ND	ND	ND
Decamethylcyclopentasiloxane	3.19 ± 2.1	ND	ND	ND
Limonene	0.215 ± 0.025	ND	ND	ND
Caffeine	0.260 ± 0.23	ND	ND	ND
2-Oxo-3-phenyl-2,3,5,6,7,8-hexahydroindolizine	40.3 ± 13	ND	ND	ND
9-Octadecenamide	5.76 ±2.5	ND	ND	ND

Notes: ND = not detected. The lower detection limit was determined from the lower detectable amount (1 ng) by GC/MS and the ND value was, on average, 9.2 ng/g.

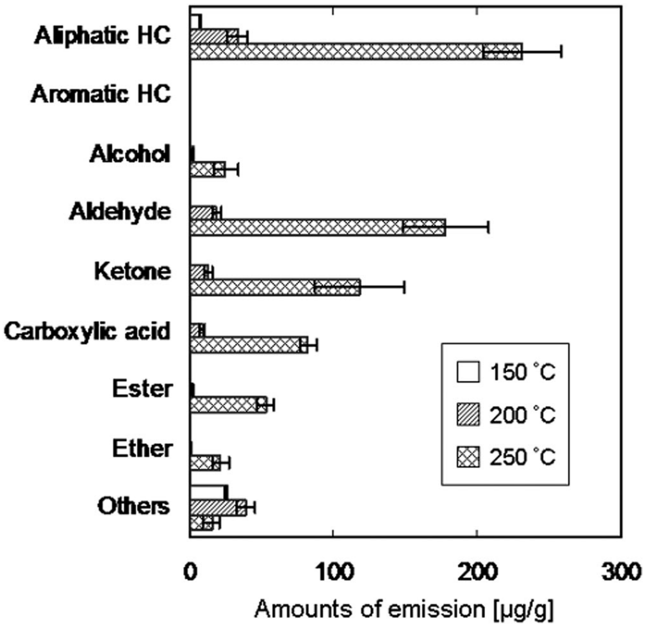

Figure 2. Amounts of VOCs (in toluene equivalent) emitted from LDPE melted at 150, 200, and 250 °C in air atmosphere.

antioxidants contained in commercial plastic products, indicating BHT might diffuse from the plastic regardless of the temperatures in this range (i.e., 150–250 °C). Because the melting and boiling points of BHT are 69–71 and 265 °C, respectively, BHT in the LDPE polymer might be simply volatilized without reacting with other compounds.

Effects of Atmosphere

Figure 3 shows total ion chromatograms (TICs) of the VOCs emitted from each plastic melted at 200 °C in air and N_2 atmospheres. There were distinct differences in the chromatograms between the atmospheres. The peak heights observed in N_2 in the early retention time were smaller than those in air, especially in LDPE and waste plastics (Figure 3, c and d). Specifically, the peaks with retention times less than 20 and 30 min for LDPE and waste plastics, respectively, were considerably smaller in N_2 than in air. According to the temperature condition of GC, these peaks likely correspond to the compounds with boiling temperatures lower than 180 and 250 °C, respectively. Because most VOCs are known to come from oxidative degradation of the polymers,[7] degradation of the polymers, a cause of VOC emissions, might be reduced under the anoxic condition. In particular, production of low-molecular-weight compounds (i.e., those with low boiling temperatures) was selectively reduced under the anoxic condition because of the shortages of oxygen molecules, which increase the probability of cleavage and fragmentation of the plastic polymers into low-molecular-weight VOCs. For PS, larger numbers of peaks in air were observed than in N_2 (Figure 3b). The peaks observed in air, but not in N_2, were found to correspond to the

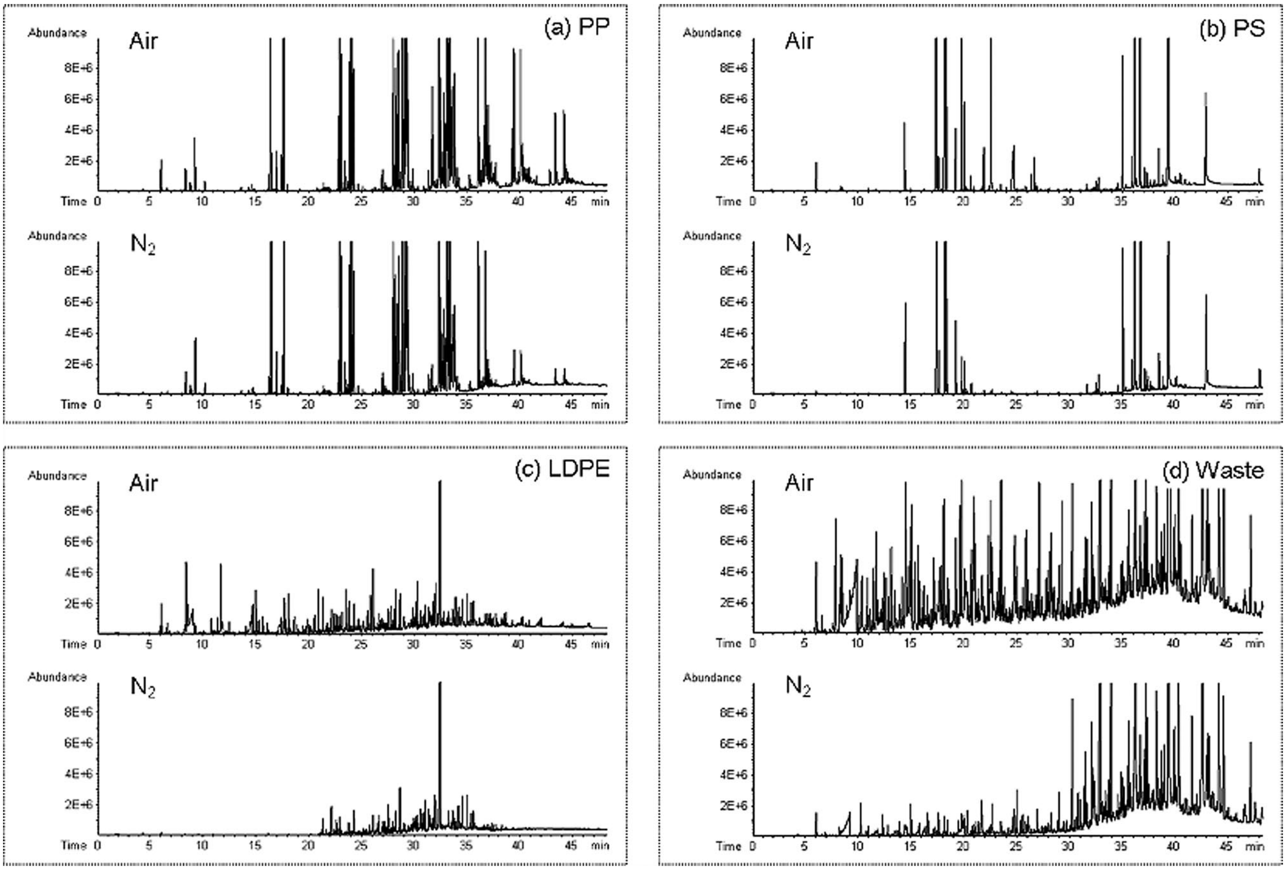

Figure 3. TICs of VOCs from (a) PP, (b) PS, (c) LDPE, and (d) waste plastic pellets melted at 200 °C in air and N_2 atmospheres.

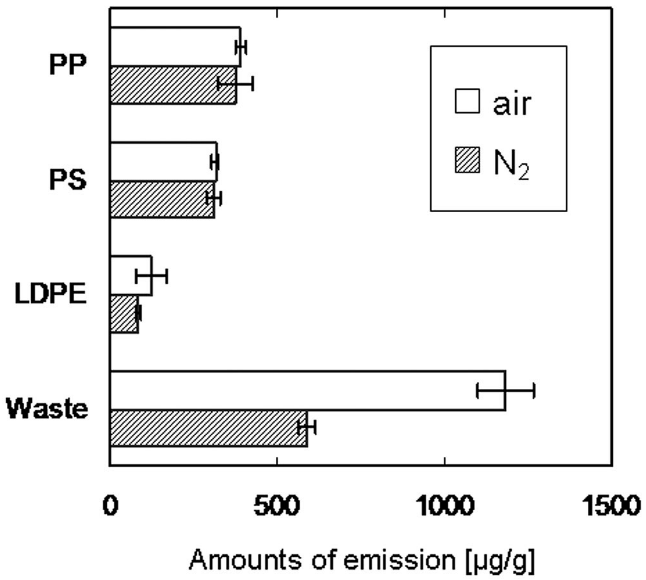

Figure 4. Amounts of TVOCs (in toluene equivalent) emitted from PP, PS, LDPE, and waste plastic pellets melted at 200 °C in air and N_2 atmospheres.

oxygenated compounds, indicating the reduction of the oxidative degradation of the polymer under the anoxic condition.

Figure 4 exhibits the amounts of TVOCs emitted from each plastic melted at 200 °C in air and N_2 atmospheres. The amounts of each functional group of VOCs emitted from each plastic melted at 200 °C in air and N_2 atmospheres are also shown in Figure 5. The results indicated the larger amounts of oxygenated compounds such as alcohols, aldehydes, ketones, carboxylic acids, and ethers in air than in N_2, resulting in the overall increases of TVOCs in air. In particular, although the detailed mechanisms are unknown, the larger amounts of oxygenated compounds, including aldehydes, ketones, and carboxylic acids, were observed for LDPE and waste plastics in air. The ratios of these compounds generated in N_2 to those in air were 2.5 and 38% for LDPE and waste plastics, respectively. Meanwhile, certain amounts of the oxygenated compounds were also emitted under N_2 atmosphere. Although future research should further elucidate the underlying mechanisms, several mechanisms are thought to cause these phenomena. For instance, oxygen molecules possibly adsorbed on the surface of the plastics during the storage might react with the polymers to generate the oxygenated compounds even in N_2 atmosphere. It is also thought that certain plastic polymers have been oxidized and fragmented to low-molecular-oxidized compounds even before the experiments because the samples were generally stored in air.

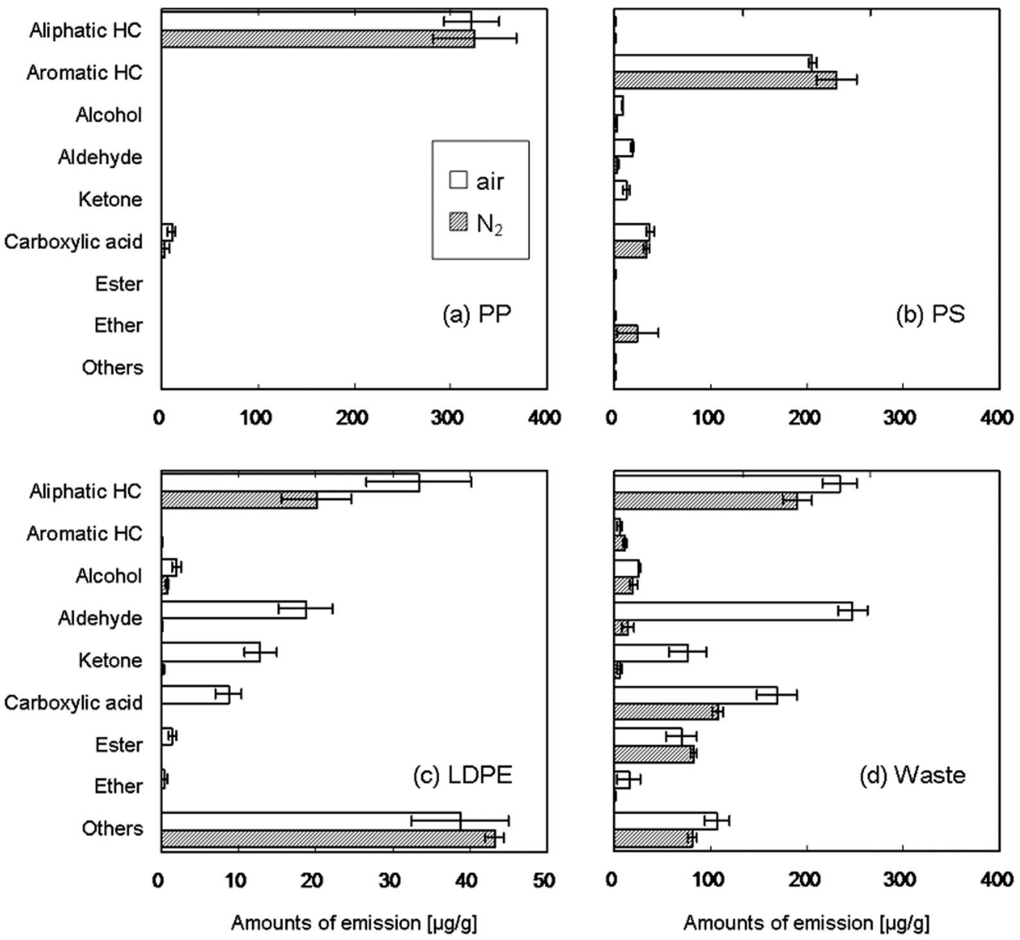

Figure 5. Amounts of each functional VOC (in toluene equivalent) emitted from (a) PP, (b) PS, (c) LDPE, and (d) waste plastic pellets melted at 200 °C in air and N_2 atmospheres.

These molecules are likely volatilized during the melting experiments of the plastics.

Compounds Originating from Other Mechanisms

Although most VOCs are expected to come from polymer degradation, several species of VOCs, those classified as "others" in particular, likely originated from mechanisms other than polymer degradation. For instance, several compounds such as BHT, a major type of antioxidant, were detected from the virgin LDPE sample. Indeed, amounts of BHT emitted from LDPE are not dependent on the atmosphere, indicating simple evaporation by heat. Moreover, small amounts of aliphatic compounds (~49.3 ± 25 and 73.5 ± 68 μg/g in air and N_2 atmosphere, respectively) were also detected even from PS, which has the structure of an aromatic polymer. According to the manufacture of the PS pellets,[9] grease additives consisting mainly of aliphatic compounds are generally used during extrusion molding of the PS pellets. Therefore, the grease applied to the pellets might cause emissions of these aliphatic compounds volatilized and/or potentially reacted with oxygen molecules in air.

Various species of VOCs unlikely to originate from thermal degradation of the polymers were identified in the VOCs from the waste plastics. For example, chlorinated HCs and phthalate compounds were identified in VOCs emitted from the waste plastics (Table 2), indicating inclusion of contaminant PVC. Phthalate compounds generally mixed in PVC resins as plasticizers are known to be potential human reproductive toxicants.[11] Moreover, the degradation of PVC can generate hydrogen chloride (HCl), which is harmful to humans, at temperatures around 200 °C.[12,13] Although HCl is not measurable by GC/MS, it might be generated from the waste plastic. Several compounds such as limonene, caffeine, siloxane, and nitrogenous compounds, which likely originate from food residues, cleaning agents, degreasers, and so on, remained in the plastics and were only detected from the waste plastic (Table 2). Thus, various potentially toxic compounds were emitted exclusively from the waste plastic.

CONCLUSIONS

In this study, the basic characteristics of the VOC emissions from melted virgin and waste plastics were investigated. The result showed the higher temperatures generated larger amounts of TVOCs. The VOCs emitted from the virgin plastic pellets likely originated from polymer degradation. Meanwhile, smaller TVOC emissions were observed in N_2 than in air. In particular, larger amounts of the oxygenated compounds, which are generally hazardous and malodorous, were detected in air than in N_2. In addition to the compounds originating from polymer degradation, the compounds originating from plastic additives were also detected from LDPE and PS. Furthermore, various species of VOCs likely originating from contaminant inseparate PVC, food residues, cleaning agents, degreasers, and so on were detected from the waste plastic. Thus, melting waste plastics, as is conducted in recycling facilities, might generate larger amounts of potentially toxic compounds than virgin plastics.

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EPB 433- Health and Environmental Effects of Burning Waste Plastics

Issue:

Consumption of plastics has steadily increased over the years due their flexibility, affordability and durability as compared to other materials with similar use. Approximately 20,000 tonnes of waste residential plastic and another 3,500 tonnes of waste agricultural plastic comprising primarily of discarded grain storage bags are generated annually in Saskatchewan. While stewardship recycling programs exists for some of the residential waste plastics, the Ministry of Environment is working with industry partners and stakeholders to establish a waste agricultural plastic recycling program especially for the discarded grain storage bags. A large fraction of waste plastics still ends up in the landfills and/or is burned unlawfully in the open by the users.

Being readily combustible, these plastics when burned under open and uncontrolled fire conditions at low temperatures generate black plumes of smoke and toxic volatilization products, which become incorporated into the ambient environment, resulting in human and environmental exposure. In addition, large amount of greenhouse gases such as methane and carbon oxides and particulate matter are emitted into the atmosphere. When garbage or refuse is burned under open-fire low temperature conditions, the waste plastics that they contain contribute to smoke generation and infuse toxic decomposition products of plastics into the smoke which can potentially cause significant health and environmental concerns.

> *"The burning of plastic grain bags releases chemicals into the air that we all breathe, causing serious lung damage and contributing to other long-term health problems. For people with lung diseases such as asthma and Chronic Obstructive Pulmonary Disease, even a single exposure to this type of smoke can worsen their disease. This can result in hospitalization, increased use of expensive medications and absences from school or work."*
>
> *.... Dr. Brian Graham, President & CEO, Lung Association of Saskatchewan*

Background Information:

Plastics are non-biodegradable. Principle types of plastics found in the waste are poly(ethylene) **PE** used in trash bags, grain storage bags and shopping bags; poly(vinyl chloride) **PVC** used in bottles, packaging and containers; poly(ethylene terephthalate) **PETE** used predominantly in beverage bottles and similar containers; poly(styrene) **PS** a light spongy material used in meat, eggs and miscellaneous product trays and hot beverage cups; and poly(propylene) **PP** used in yogurt containers, straws, margarine tubs and special bags. Most of these plastics are discarded after single use and become garbage.

The manufacturing of plastics involve various chemical processes and utilizes variety of chemical compounds and additives including phenols, amines and esters, antioxidants, UV and light stability improvers, antistatic agents and heat stabilizers that impart the finished product specific characteristics for its intended use.

The finished product that is the plastic itself is environmentally quite stable. However, the additives, their chemical reaction and degradation products incorporated into the polymeric material have the potential to be released into the environment and cause significant health and environmental concerns[i].

Pollutants generated from burning of Plastics & related health effects:

The byproducts of plastic combustion are airborne particulate emission (soot) and solid residue ash (black carbonaceous colour). Several studies have demonstrated that soot and solid residue ash possess a high potential of causing significant health and environmental concerns. The soot when generated is accompanied with volatile organic compounds (VOCs), semi-VOCs, smoke (particulate matter), particulate bound heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs) and dioxins[ii] and has the ability to travel thousands of kilometers, depending on prevailing atmospheric conditions, before it can drop back on earth and enter into the food chain. Further, the composition of byproducts of plastic combustion as to their type and concentration depends on the combustion temperature and the flame residence time.

The toxicity of combustion products generated from burning of plastics has been evaluated by various researchers under experimental conditions. Significant amount of pollutants of environmental and health concern including carcinogens such as PAHs, nitro-PAHs and dioxins have been identified in the airborne particulate emissions. Further, these particulates have been found to be highly mutagenic[iii]. PAHs in the range of 8-340 ppm have been observed in the soot which is significant enough to cause cancer[ii]. Researchers have also found high concentration of persistent free radicals (unstable and highly reactive molecules) both in the soot and the solid residual ash which are considered to be very important in the creation of adverse health effects especially to human lungs[v].

A study of the combustion of PE (both low (LDPE) and high density (HDPE) polyethylene) at different operating conditions detected more than 230 VOCs and semi-VOCs especially olefins, paraffin, aldehydes and light hydrocarbons[ii]. Amongst VOCs, benzene is a known carcinogen and has been observed to be released in significant quantity during plastic combustion. Some of the toxic semi-VOCs including benzo(a)pyrene and 1,3,5 trimethylbenzene have also been observed in significant quantities in the emissions from plastic combustion[iv].

Heavy metals including lead, cadmium, chromium and copper have been measured in the smoke and the solid residue ash[ii]. DEHP is one of the compounds among the plasticizers used in plastic manufacturing that has been described by USEPA as a probable human carcinogen, a potential endocrine disruptor and is believed to be harmful by inhalation, generating possible health risks and irreversible effects[v]. This compound is also released during the combustion of plastic. Most of the pollutants discussed have the potential to cause health and environmental effect as discussed in the table below.

Potential pollutant generated from burning of Plastics	Health Effects	Environmental Effects
Carbon Monoxide	Causes dizziness, headaches and slowed reflexes. Affects mental function, visual acuity and alertness	Oxidized to carbon dioxide (which is a greenhouse gas) in the atmosphere
Dioxins and Furans	May cause cancer; causes growth defects; affects DNA; affects immune and reproductive systems	Increased toxic loading on environment; leads to contaminated water/land, affects animal health
Polynuclear Aromatic Hydrocarbons (PAHs)	Cancer causing agent in most animal species including mammals, fish and birds	Increased toxic loading on environment, leads to contaminated water/land, affects animal health
Volatile Organic Compounds (VOCs)	Directly toxic including problems ranging from cancer risks to nervous disorders. Causes respiratory irritation/illness, chronic lung disease	Contributes to low level ozone (smog), causes vegetative damage. Leads to contaminated water/land, affects animal health
Particulate Matter (PM)	Irritation of respiratory tract, aggravated asthma, contributes to chronic obstructive pulmonary disease	Increased toxic loading on the environment; leads to contaminated water/land and affects animal health
Aldehydes	This is a animal carcinogen. Causes eye and respiratory illness and headaches	Increased toxic loading on environment, leads to contaminated water/land, affects animal health

With the above discussion, it is worth emphasizing that open uncontrolled burning is by no means an environmentally sound option to dispose of waste plastics including waste agricultural plastics such as discarded grain storage bags. Other environmentally sound options must be explored for their safe disposal and/or recycling.

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