J. Pack. Sci. Tech. Vol.8 No.6 (1999)

Review

Endocrine Disruptor Screening and Testing : The U. S. Approach

G. E. Timm, A. F. Maciorowski

Office of Prevention, Pesticides, and Toxic Substances
U. S. Environmental Protection Agency
Washington, DC 20460

Over the past five years, endocrine disrupting chemicals have emerged as a major environmental science and policy issue. Documented effects to fish and wildlife populations, coupled with evidence from human poisonings, epidemiology, and experimental toxicology have led to an emerging hypothesis that chemicals may be affecting reproduction and development. In response to these concerns, the U. S. Congress passed the Food Quality Protection Act (FQPA) and the Safe Drinking Water Act (SDWA) Amendments of 1996. The FQPA requires EPA to screen pesticides for estrogenic effects on human health and permits EPA to screen chemicals found in drinking water sources for other hormonal effects. Faced with implementing a new regulatory program, EPA responded by sponsoring focused research to better understand the basic science of endocrine disruption, and by establishing the Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) to advise the Agency on the design of an endocrine disruptor screening program. EPA is currently implementing a screening program based on EDSTAC's recommendations.

1. INTRODUCTION

Scientific evidence has accumulated that humans, domestic animals, and fish and wildlife species have displayed adverse impacts from exposure to chemicals that interact with the endocrine system [1, 2]. To date, such problems have been best documented in humans, and domestic and wildlife species that have been exposed to high concentrations of organochlorine compounds (e.g., DDT and its metabolite DDE, PCBs, and dioxins), and to a few naturally occurring plant estrogens [3]. Numerous reports indicate a variety of compounds can modulate the endocrine system and affect reproduction and development in invertebrates, fish and wildlife. However, few examples are currently available that establish the extent to which these insults have resulted in adverse population responses[4]. It is also unclear, whether adverse effects in the human population at-large can be attributed to environmental concentrations of contaminants operating through endocrine modulation. Conflicting reports regarding declines in the quality and quantity of sperm production in humans have been published [1]. Although reported increases in cancers of endocrine sensitive tissues (e.g., breast, prostate, testicular) are clear, there is little direct evidence linking disease trends with exposure to environmental pollutants. An endocrine-related basis for such effects is plausible, but considerable scientific uncertainty exists. Nevertheless, there is little doubt that small disturbances in endocrine function, particularly during certain highly sensitive stages of the life cycle (e.g., development, pregnancy, lactation), can lead to profound irreversible adverse effects [3, 4].

Taken collectively, the body of scientific research on human epidemiology, laboratory animals, fish and wildlife provides a plausible scientific hypothesis that environmental contaminants can disrupt the endocrine system leading to adverse health consequences. A critical issue is whether ambient environmental concentrations are sufficiently high to exert adverse effects on the general population. Epidemiology, mammalian toxicology, and ecological toxicology investigations are all necessary to resolve the fundamental scientific questions and uncertainties surrounding the endocrine disruptor issue.

The U. S. has implemented a two-part approach to endocrine disrupters. The first is a research program to increase understanding of the basic scientific issues concerning endocrine disruption. The second, the subject of this paper, is a regulatory screening and testing program to identify and characterize the effects of endocrine disrupting chemicals.

2. ENDOCRINE DISRUPTOR SCREENING PROGRAM

Faced with increasing concern over endocrine disrupting chemicals and adverse human health outcomes, the U. S. Congress passed two laws that contained provisions for screening chemicals for their potential to disrupt the endocrine system. The Food Quality Protection Act of 1996 (P. L 104-170), 21 U.S.C. § 346a(p)) requires EPA to :

> "develop a screening program using, appropriate validated test systems and other scientifically relevant information, to determine whether certain substances may have an effect in humans that is similar to an effect produced by a naturally occurring estrogen, or such other endocrine effect as the Administrator may designate."

When carrying out the screening program, EPA (A) "shall provide for the testing of all pesticide chemicals" and (B) "may provide for the testing of any other substance that may have an effect that is cumulative to an effect of a pesticide chemical if the Administrator determines that a substantial population may be exposed to such a substance." 21 U. S. C. § 346a(p)(3). In addition, Congress amended the Safe Drinking Water Act (42 U. S. C. § 300j-17) authorizing the EPA to screen contaminants in drinking water to which substantial numbers of people would be exposed.

The congressional mandate to develop a screening program in a controversial and rapidly emerging area of science led EPA to establish The Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC) in October 1996. The EDSTAC was charged with advising the Agency on the development of a practical, scientifically defensible endocrine disruptor screening strategy. The EDSTAC consisted of 39 members representing the pesticide and chemical manufacturers, state and Federal government, and environmental and public health advocacy organizations.

At its first meeting, EDSTAC expanded the scope of its deliberations to include potential effects on the androgen and thyroid systems in addition to estrogen. The Committee cited numerous examples of anti-androgen and anti-thyroid agents and the impact that these systems have on reproduction, growth and development as reasons for their inclusion. Ecological effects were also deemed important in that ecological effects have provided the strongest evidence of endocrine disruption to date. Finally, EDSTAC also included chemicals other than pesticides and drinking water contaminants as candidates for screening and testing. The universe of candidate chemicals under consideration included approximately 900 pesticide active ingredients ; 2,500 pesticide formulation inert ingredients ; 75,500 industrial chemicals ; and 8,000 cosmetics, food additives and nutritional supplements [5].

The overall frame work that EDSTAC recommended consists of four major steps : (1) initial sorting of chemicals, (2) establishment of screening priorities, (3) Tier 1 screening, and (4) Tier 2 testing. The initial sorting step was intended to separate the chemicals into four discrete categories. Category 1 consists of polymers with a numerical average molecular weight (NAMW) greater than 1,000 daltons and certain exempted chemicals that are unlikely to display endocrine activity (e.g. , certain biologically inactive ingredients or highly reactive substances such as strong mineral acids and bases that will react at the portal of entry). Polymers with the specified NAMW will be set aside pending a review of their monomers. Such polymers were thought to pose little risk because, they are generally too large to pass through biological membranes and interact with the endocrine system. Polymers that are identified as posing a potential risk because of their monomers or additives will probably be evaluated through leaching and stability studies rather than whole animal toxicity studies. Category 2 consists of chemicals with insufficient data to determine their potential for endocrine activity. Category 3 includes those chemicals that have sufficient data to bypass screening, but need testing. Finally, Category 4 consists of substances with adequate data which will be referred to the appropriate agency for hazard assessment.

2.1 Priority Setting

The largest category of chemicals, and that of greatest interest to EPA concerning screening, are those chemicals with insufficient information and data (Category 2). EDSTAC considered several different approaches for setting priorities among these chemicals. One consisted of ranking chemicals with known exposure and effects as the highest priority for screening and testing. EDSTAC was concerned, however, that such an approach would focus attention on the most studied chemicals, resulting in a low priority for chemicals that were little studied. The Committee also recognized that priority setting is not generally an objective, data-driven process. Comparable, equitable, and uniform data are simply not available for the majority of commodity chemicals. As an example, ranking a chemical that has extensive monitoring data in wildlife against one known to have human exposure, but entirely lacking effects data in mammals, is not a simple task. The Committee wanted a system in which like information and data could be compared in priority setting, but one that was also subject to clearly stated value judgments to ensure public confidence. The approach recommended by EDSTAC was termed a "compartment-based" priority setting strategy.

In the compartment-based strategy, a number of compartments (or sets) of chemicals are defined and the individual chemicals within each set are prioritized. One might think of mathematics and sets of numbers as an analogy. In mathematics one could define sets of real numbers, integers, irrational numbers, even numbers, etc. Numbers within each set could then be ordered in some fashion. Some numbers obviously belong to more than one set, and the same will hold true for chemicals. One could define a set of high production volume chemicals, chemicals measured in biota, chemicals in consumer products, chemicals detected in the workplace, etc., and then prioritize the chemicals within each group. Given the large number of chemicals that must be prioritized for screening, implementation will undoubtedly occur in phases or batches. Once the sets of chemicals are defined and prioritized, a batch of chemicals will be selected for the initial phase of the screening program. The contribution of each set of chemicals to this batch is the key subjective judgment that must be made in the priority setting process. The size of the first batch and spacing of subsequent batches of chemicals depends largely on the available laboratory capacity of the system, the ability of industry to pay for testing, and the resources of the EPA to review submitted data.

Although EDSTAC did not reach agreement on the definition or weighting of specific compartments, EDSTAC listed the following categories and specific kinds of information that should be considered in developing the compartment-based approach.

A. Exposure-Related Information

1. Biological sampling data
2. Environmental, occupational, consumer product, and food-related data (sampling and/or use data)

3. Environmental releases
4. Production volume
5. Fate and transport data and models

B. Effects-Related Information

1. Toxicological laboratory studies and databases
2. Epidemiologic and field studies and databases
3. Predictive biological activity or effects models (e.g. Structure Activity Relationships [SAR] and Quantitative Structure Activity Relationships [QSAR])
4. Results of high throughput pre-screening (HTPS)

C. Integrated Effects and Exposure Information

D. Specially Targeted Priorities

1. Mixtures
2. Naturally Occurring Non-Steroidal Estrogens
3. Nominations

Following the basic framework and guiding principles laid out in the EDSTAC report, EPA developed an initial "strawman" proposal for a compartment-based system which was presented at a public workshop [6]. The proposed approach assumes that a database will be developed to contain the rank-ordered lists of chemicals within each compartment as well as the weights and algorithms to select chemicals for entry into tier 1 screening.

EDSTAC also recognized other problems for priority setting. Few chemicals actually have data that directly measures their endocrine disrupting potential. Most chemicals have scant effects data. Often these data are limited to short-term mutagenicity tests and acute toxicity in rodents. Even chemicals that have been examined with respect to reproduction and developmental effects were likely tested using conventional protocols that have not been specifically designed to detect endocrine effects. EDSTAC believed that the most expedient means for obtaining useful endocrine effects data was to employ high throughput screening technology (HTPS) to high production volume chemicals and pesticides. The first two in vitro assays recommended by EDSTAC may, in fact, be conducted in a high throughput mode. These assays are specific to receptor binding modes of action. However, all 15,000 high production volume chemicals could theoretically be assayed in approximately 3 to 6 months at a relatively modest cost. This information could be used with production and exposure information and data to assist priority setting for further screening. A positive result in the high throughput screen would raise the priority for testing a substance relative to its priority based purely on production and exposure. Concomitantly, a negative in the high throughput screen would neither raise nor lower the priority since a chemical could be endocrine active through mechanisms other than receptor binding.

2.2 Tier 1 Screening

EDSTAC built upon the work of other expert workgroups in reviewing candidate assays for a screening system [7,8]. These expert groups reviewed a number of individual assays and concluded that a battery of assays was necessary to evaluate endocrine disruption potential. They further recommended that the battery include *in vitro* and *in vivo* assays. *In vitro* assays are advantageous in that they are inexpensive and specific for a particular mode of action. Conversely, they lack the metabolic and response complexity of intact animals. EDSTAC recommended a battery of three *in vitro* assays and five in vivo assays for Tier 1 screening. The *in vitro* assays include an estrogen receptor binding or reporter gene assay, an androgen receptor binding or reporter gene assay, and a steroidogenesis assay using minced testes. EDSTAC preferred functional assays over receptor binding assays because the former can be used to differentiate agonist from antagonist activity, and they are also more sensitive than the latter [5].

The *in vivo* Tier 1 assays are :

Rodent 3-day Uterotrophic Assay
Rodent 20-day Pubertal Female Rodent Assay with Thyroid
Rodent 5-7 day Hershberger Assay
Frog Metamorphosis Assay
Fish Reproductive Screen

Deliberate endpoint complementarity is incorporated into the screening battery, and the assays in the battery are meant to work together as a whole. Thus, the ER reporter gene, uterotrophic and pubertal female assays screen for estrogenicity and anti-estrogenicity. The AR reporter gene and Hershberger assays screen for androgenicity and anti-androgenicity. The frog assay and pubertal female assays screen for thyroid. The fish assay is mainly present because fish are the class of vertebrates most distant from the mammals in terms of their metabolism and hormone systems. Having diverse taxa in Tier 1 may provide some idea of when we can be confident of consistent results among organisms and when we must be concerned about variability. A weight of the evidence approach will be used to evaluate the results in Tier 1. *In vivo* results will outweigh *in vitro* results. Chemicals testing negative in Tier 1 would be regarded as having low potential for interaction with the estrogen, androgen or thyroid systems. Chemicals testing positive would proceed for more in depth evaluation in Tier 2.

In addition to the assays listed above, EDSTAC recommended that EPA standardize and validate several alternative assays. These are the pubertal male, *in utero* assay and aromatase assay. If the pubertal male assay is successful, it could replace the pubertal female, Hershberger and steroidogenesis assays but the aromatase assay would have to be added since males are not a good model for studying aromatase. The *in utero* assay could potentially replace all of the mammalian in vivo assays since it embraces all potential modes of action [5].

2.3 Tier 2 Testing

The Tier 2 tests are meant to identify adverse effects due to endocrine disruption and to establish a relationship between dose and response. The criteria identified by EDSTAC for Tier 2 tests was that the most sensitive life stage be tested (in utero or in ovo), that the tests be multi-generational and that each major taxonomic group be represented. Thus EDSTAC recommended five multi-generation tests : one each in mammals, birds, fish, amphibians and invertebrates. In theory, Tier 2 can be tailored based on both exposure and effects information. For instance, if it can be shown that only exposure to humans will occur, only the 2-generation test in rodents will be required. Unfortunately, the limited number of species represented in Tier 1 makes it unlikely that one will have sufficient information to tailor the Tier 2 test menu on the basis of Tier 1 results alone.

3. EPA IMPLEMENTATION

EPA is currently implementing EDSTAC's recommendations. EPA published a notice in the Federal Register on December 28, 1998, to obtain comments on its proposed screening program and implementation plans. The proposed screening program and the implementation plan were peer reviewed by the EPA Science Advisory Board and FIFRA Scientific Advisory Panel in March 1999.

3.1HTPS

A pilot demonstration of HTPS was completed in March 1999 to determine the suitability of the assay system for commercial chemicals and pesticides. Both stable and transient transfected reporter gene constructs were prepared based on T47D cells for the estrogen receptor (ER), MDA 453 cells for the androgen receptor (AR), and HeLa cells for the thyroid receptor (TR). The goal of identifying weak agonists and antagonists for ER, AR and TR was never realized due to low signal to noise ratio caused by less than optimal induction and well-to-well cross talk.

EPA decided to widen its search for an HTPS system. It will try to identify an off-the-shelf technology for HTPS and could proceed with HTPS if this new effort is successful. If HTPS is not shown to be a feasible approach, EPA may rely on the use of quantitative structure activity relationships (QSARs) to meet the objective of a quick way to provide an indicator of potential hormonal activity of unknown chemicals for priority setting purposes.

3.2 Standardization and Validation

The Food Quality Protection Act also states that the screens and tests be validated to ensure that they give reliable and repeatable results. A task force has been established in the U.S. to coordinate the standardization and validation effort among government, industry and public interest groups.

International standardization and validation efforts are being conducted separately from U.S. domestic efforts. Through its Test Guidelines Program, OECD has established the Endocrine Disruptor Testing and Assessment Task Force. Laws, regulatory processes, and regulatory procedures differ in the United States, Japan and Europe. Thus, while EPA actively participates as a member of OECD, the OECD Test Guidelines Program, and the OECD Task Force, separate domestic and international activities are necessary. Although international activities are distinct from the U.S. task force activities, there is overlapping membership to ensure appropriate liaison and communication, eliminate unnecessary duplication of effort, and facilitate international harmonization, where appropriate.

The general validation framework we envision for endocrine disruptor screens and tests follows the general process and stages developed by the U.S. Interagency Coordinating Committee for the Validation of Alternative Methods (ICCVAM) and will proceed in six major stages : 1) Research and assay development 2) demonstration of relevance and standardization 3) interlaboratory validation 4) scientific peer review ; 5) An independent scientific peer review ; and 6) Agency regulatory approval, wherein we consider the peer review comments and recommendations and make a decision on the regulatory acceptability (or need for additional work) of the method in question [9].

EPA will initially place a higher priority on standardizing and validating the mammalian assays used to assess health hazard and risk because The Food Quality Protection Act and the Safe Drinking Water Act are explicitly directed toward protecting food and drinking water to safeguard human health. The ecotoxicological screens or tests remain important because EPA cannot evaluate ecological hazard and risk on the basis of mammalian tests alone. EPA will develop and evaluate the screens and tests using a phased approach with resources allocated especially for endocrine disruptor screening and testing validation. Resources will be conserved by carefully selecting the chemicals to be used in the standardization and validation program. It is estimated that two years will be required to standardize and validate the screens and perhaps up to five years will be required for some of the newer tests.

4. CONCLUSIONS

Many policy issues in the United States and abroad will be decided before the resolution of all scientific questions. Nevertheless, we see that the results of screening and testing and the answers to many of the questions posed by the research agenda will combine to form our conclusions regarding the level of risk that endocrine disruptors pose to humans and wildlife. Ultimately in the United States, risk management actions will be taken under current U.S. laws - laws that are mainly risk based and, therefore, which require the integration and interpretation of effects and exposure data.

References

[1] *European Workshop on the Impact of Endocrine Disruptors on Human Health and Wildlife* ; EUR 17549 ; European Commission : Brussels, Belgium, 1996.

[2] *Expert Workshop on Endocrine Modulators and Wildlife : Assessment and Testing*, Tatters field, L., Matthiessen P, Campbell P, Grandy N., Lange R., Eds.; SETAC-Europe ; Brussels, Belgium, 1997.

[3] Kavlock R., Daston G., DeRosa C, Fenner-Crisp P., Gray E., Kaattari S., Lucier G., Luster M., Mac M., Mackzka C, Miller R., Moore J., Rolland R., Scott G., Sheehan D., Sinks T., Tilson H., *Environmental Health Perspectives*. 1996, 104, 715-740

[4] *Special Report on Environmental Endocrine Disruption : An Effects Assessment and Analysis*. Environmental Protection Agency : Washington, DC, EPA/630/R-96/012, 1997.

[5] *Endocrine Disruptor Screening and Testing Advisory Committee :* Final Report ; Environmental Protection Agency : Washington, DC , 1998. Available at littp://www. epa. gov/scipoly/oscpendo/history/

[6] *Strawman" Priority Setting Process for Endocrine Disruptor Screening and Testing*, Environmental Protection Agency, January 7, 1999. Available at http: //www. epa. gov/ scipoly/oscpendo/strawman. htm

[7] Ankley G., Mihaich E., Stahl R., Tillit D., Colborn T., McMaster S.. Bantle J., Campbell P., Denslow N., Dickerson R., Folmar L., Fry M., Giesy J., Gray E., Guiney P., Hutchinson T., Kennedy S., Kramer V., LeBlanc G., Mayes M., Nimrod A., Patino R., Peterson R., Purdy R., Ringer R., Thomas P., Touart L., Van Dei Kraak G., Zacharewski T. , *Environmental Toxicology and Chemistry*. 1998, 17, 68-87.

[8] Gray E., Kelce W., Weis T., Tyl R., Gaido K., Cook K., Klinefelter G., Desaulnier D., Wilson E., Zacharewski T., Waller C, Foster P., Laskey J., Giesey J., Laws S., Mclachlan J., Breslin W., cooper R., Di Giulio R., Johnson R., Purdy R., Mihaich E., Safe S. , Colborn T., et al *Reproductive Toxicology*. 1997, *11*, 719-750.

[9] *Validation and Regulatory Acceptance of Toxicological Test Methods*, A Report of the ad hoc Interagency Coordinating Committee on the Validation of Alternative Methods, NIH Report Number 97-3981 , National Institute of Environmental Health Sciences, Research Triangle Park, NC 27709. March 1997.

J.Pack.Sci. Tech. Vol.8 No.6 (1999)

Review

Safety of Food Packaging Materials

Vanee Komolprasert, Ph.D.

Division of Food Processing and Packaging, US Food and Drug Administration,
National Center for Food Safety and Technology,
6502 S. Archer Road, Summit-Argo, Illinois 60501, USA

The International Packaging Seminar (IPS'99)
June 29, 1999

Abstract

This paper will focus on two studies that are directly related to the safety issues of food packaging materials. The first study determined whether the secondary recycled polyethylene terephthalate (PET or PETE) was suitable for direct food contact applications. The second study determined the effects of gamma and e-beam radiation on food packaging intended for use with prepackaged irradiated foods.

In the first study, the test protocol suggested by the FDA (FDA, 1992) for the chemical recycling processes was used. The test protocol suggested the use of several surrogate chemicals with different physical and chemical properties to simulate the chemical contaminants that may be present in the recycled PET. These chemical contaminants could be introduced to the materials via misuse of the PET bottles for temporary storage of chemicals such as gasoline, used motor oil, and household insecticides. The experiments involved spiking virgin PET materials with these chemicals, and subjecting the contaminated PET to secondary (physical) recycling processes (aqueous-based washing, thermal drying and extrusion remelting). The efficacy of the selected recycling process conditions on removal of the surrogates from the PET and the potential migration of these chemical residues from the post-treatment PET into food simulating solvents were determined.

The second study is ongoing. Food packaging materials of commercial interest have been selected as a model, irradiated with gamma and electron beam radiation at various irradiation conditions and stored at various storage conditions. Volatile and nonvolatile compounds that are present in the test materials before and after irradiation were analyzed and compared for the effect of irradiation on the test materials. Analytical methods and some initial research results for evaluating the suitability and safety of the food packaging materials intended for prepackaged irradiated foods will be included.

I. Recycled Polyethylene Terephthalate (PET) Food Containers

PET was the first polymer among other recyclable thermoplastics to be chosen by resin manufacturers to examine its potential for recycling. Since the virgin PET polymer is synthesized by a condensation polymerization reaction, a reverse reaction (hydrolysis, methanolysis or glycolysis) is employed to convert the post-consumer PET material to initial reactants or monomers. The monomeric products are then purified prior to resynthesis to polymeric PET material. These chemical processes based on depolymerization and repolymerization have been tested using the test protocol suggested in the FDA's guidelines. The test results indicated that they are adequate for removal of certain contaminants from recycled PET and consequently, the regenerated PET material is suitable for food use. Several of these chemical processes have been carefully reviewed by the FDA prior to a no-objection letter given to the manufacturers. By 1992, at least three PET resin manufactures had received the no-objection letter.

Although the above chemical processes were successfully developed to recycle PET for food use, they are energy intensive and costly. These processes make the regenerated PET less competitive with the virgin material. Therefore an alternative, such as a physical process that is simpler and less expensive, has been considered. Several PET recyclers have attempted to develop a physical process that effectively generates post-consumer recycled PET food container suitable for food use. Prior to 1991 there were no reported physical PET recycling processes which would regenerate PET suitable for food use. Therefore, a study on the effects of physical recycling processes on PET food containers was initiated in 1991 at NCFST.

Experimental

Surrogates: At least five surrogates with various physical and chemical properties were selected according to recommendations in the FDA's guidelines (FDA, 1992). The selected surrogates were benzene (volatile, non-polar), butyric acid (volatile, polar), malathion and diazinon (non-volatile, polar), dodecane (C12), octadecane (C18), tetracosane (C24) and lindane (non-volatile, non-polar), and copper II ethyl hexanoate (heavy metal).

PET material: Specially blow-mold 2 L clear PET bottles made of virgin resins with round bottom and no cap or base cup were used. They were pre-chipped prior to use. The PET chips were experimentally spiked with each surrogate that was dissolved in an appropriate solvent at predetermined concentrations before analysis and subsequent recycling processes.

Analytical Methods of Surrogates in PET: Volatile organic surrogates were analyzed by dynamic (purge/trap) and static headspace gas chromatography (HS/GC) with flame ionization detection, or polymer total dissolution using trifluoroacetic acid (TFA) solvent followed by liquid-liquid partition (Komolprasert et al, 1994; Komolprasert and Lawson, 1994 and 1995). Nonvolatile organic surrogates were analyzed by total polymer dissolution using hexafluoro-isopropanol or trifluoroacetic acid mixed with methylene chloride followed by polymer precipitation and purification before quantification by GC with appropriate detectors (Komolprasert and Lawson, 1995 and Komolprasert et. al, 1995). Copper was analyzed using dry ashing with modifications of the AOAC method (AOAC, 1990; Komolprasert Lawson, 1995).

Aqueous-based Washing: Commercial cleaning processes are proprietary and vary between recyclers; however, most recyclers use aqueous-based washing with addition of chemicals such as detergent and caustic soda. The design of a washing process that simulates an actual process was made using the limited information published and personal communication with few recyclers. Although all commercial processes are continuous, batch washing was selected for this study due to its simplicity and ease of controlling process parameters during washing. The chosen washing conditions were 1% Triton X-100 surfactant in water maintained at 90°C for 20 min with 600 rpm mixer speed (Komolprasert and Lawson, 1994), followed by deionized water rinse at 70-80°C for 15 min, filtered with a sieve shaker, and thermally dried using an IR lamp for 20 min or until dried PET flakes were obtained.

Thermal Drying: Small-scale drying experiments were conducted using a lab muffle furnace. In the experiments, the washed, spiked PET chips were placed in the furnace maintained at 160-170°C for 4 h to simulate the desiccant dryer used commercially. The concentrations of surrogates remaining in the dried flakes were subsequently determined using the analytical methods developed at the NCFST. The drying conditions used in this study significantly reduced amount of most surrogates except copper from washed spiked PET chips (Komolprasert and Lawson, 1995).

Extrusion Remelting: The extrusion conditions for a Haake single screw extruder selected for generating PET sheets was as follows: temperature gradient from feed zone to die zone 260-290°C, die gap of 2 mm, and vented screw speed of 20 rpm. An average throughput rate was 31-32 g/min. The results obtained indicated that the remelting removed significant levels of some surrogates from washed and dried spiked PET chips but the levels varied with the type and residual concentrations of the surrogates adsorbed on or absorbed in polymer matrix. Regardless of the concentrations, the remelting did not have a significant effect on lindane or copper (Komolprasert et. al., 1996).

Analytical Methods of Surrogates in Food Simulating solvents: The analytical methods for quantifying the surrogates in 8% ethanol/water and in heptane were modifications of those used for quantitation of the surrogates in the PET polymer (Komolprasert and Lawson, 1997; Komolprasert et al., 1997).

Migration: PET sheets were made from PET chips that had been spiked with various surrogates, washed and dried prior to extrusion remelting. The Haake single screw extruder was used to produce extruded PET sheets with an average thickness in a range of 0.23-0.30 mm. The sheets had low crystallinities in a range of 6-15% as compared to 31% for 2-L PET bottle wall (Komolprasert et al., 1997). The residual concentrations of the surrogates in the sheets was determined before they were used in subsequent extraction experiments in 8% ethanol/water or heptane (FDA, 1993a). Concentrations of surrogates in the extracted PET strips and food simulants were determined, and compared to the 0.5 ppb threshold limit (Komolprasert et. al., 1997). The extraction data suggest that residual contaminants (surrogates) present in the PET at levels ranging from 0.6 ppm benzene to 24 ppm copper salt migrated into food simulants at concentrations lower than 10 ppb. This suggests that at these levels of residual contaminants the recycled PET may be acceptable for food-contact use.

Results

The results from small scale washing and drying experiments indicated that the surrogates were reduced significantly but the efficacy depends on surrogate type, and initial concentration and washing conditions. Washing at 90°C with 1% nonionic surfactant (Triton X-100) tends to remove most of non-polar, non-volatile organics from the PET. Intensive drying at 160-170°C for 4 h removes most volatile compounds (benzene and butyric acid) from the PET. The drying also removes C12 and C18 and non-volatiles (C24, malathion, diazinon and lindane) from the PET. The results from extrusion experiments indicate that there is additional effect of extrusion remelting on removal of some surrogates being present in the recycled PET at high concentrations except lindane and copper salt.

Although the concentrations of the residual contaminants in the washed, dried, and extruded PET chips generated in this study were still high, the migration of these contaminants from the PET into the aqueous ethanol and heptane food simulating solvents occurred at concentrations lower than 10 ppb. The 10 ppb limit is calculated using assumptions from "Points to Consider" document (FDA, 1992) and it is the maximum allowable concentration of the residual contaminant in the food simulant which will not exceed the dietary concentration of 0.5 ppb (FDA, 1993b and 1995).

Based on the data obtained in this study, it can be concluded that it is possible to develop a physical recycling process that is effective for regeneration of PET suitable for direct food-contact uses. As long as PET is still a high demand in the market, more recyclers will attempt to develop other physical recycling processes that are more economical than the existing ones. It is noteworthy that this study did not consider changes of physical and mechanical characteristics in recycled material which are also important in determining if the recycled PET provides the functionalities required by the product.

II. Effects of Gamma and Electron-beam Irradiation on Food Packaging Materials

Irradiation is an effective technology for reduction and elimination of foodborne pathogens in foods, only of particular interest for those that are prepackaged prior to irradiation to avoid recontamination. Irradiation for food just recently received an increased interest after red meat irradiation was approved by the FDA (FDA, 1997). In the irradiation process of prepackaged foods, the package itself could potentially undergo chemical changes, which include cross-linking and degradation. The chemical compounds initially present or the degradation products formed upon irradiation that could migrate into food at storage conditions are a potential safety concern. As a result, a premarket safety evaluation of the material is required by the FDA. Most of the current permitted packaging materials were approved in the 1960's.

In general, the chemistry of gamma and electron beam (e-beam) irradiation is indistinguishable in interactions with foods and microorganisms according to laboratory data. At a given dose permitted by the FDA, both techniques are indistinguishable in efficacy relative to reduction of microbial load on food without significant changes in food qualities. The chemical changes and migration characteristics of the radiolytic products formed in newer packaging materials are lacking. The lack of modern materials approved for use during irradiation has been cited as one of impediments to large-scale implementation offood irradiation for control of foodborne pathogens in foods. Selection of packaging materials for use in food irradiation depends on the resistance or stability of the material to chemical changes when irradiated at commercial doses. These chemical changes are dependent on irradiation conditions, packaging and post-irradiation treatments. At a given dose the e-beam processing deposits the ionizing energy to the material at a faster rate than gamma radiation, often resulting in less oxidative degradation and improved performance of polymer packaging. Although gamma radiation is currently the most common process, the use of e-beam technology is emerging and therefore, the packaging materials for e-beam should be investigated prior to use.

Experimental

Test Materials: A soaker pad and four semi-rigid polyethylene terephthalate materials were used. The soaker pad is usually used to absorb exudate of uncooked meat, poultry, pork, and seafood, and it is comprised of cellulose and polyethylene (PE). The PET materials are: (1) Crystalline and oriented PET homopolymer with 1.36 g/ml density, 25% crystallinity, and 0.30-0.33 mm in thickness. (2) Crystalline and oriented PET with 1.5 mole % isophthalic acid comonomer, 1.37 g/ml density, 30% crystallinity, and 0.28-0.30 mm in thickness. (3) Amorphous and nonoriented PET copolymer with 3 mole % cyclohexanedimethanol and 1.5% di-ethylene glycol, 1.33 g/ml density, 5% crystallinity, and 0.25-0.28 mm in thickness. (4) Amorphous and nonoriented PET copolymer with 31 mole % cyclohexanedimethanol, 1.33 g/ml density, less than 2% crystallinity and 0.25-0.28 mm in thickness.
The test material was pretreated to remove organic residues before placing in 20-ml headspace glass vials or 250 ml glass Jar. The HS vial was purged with ultra pure nitrogen before closing with aluminum lined silicone septum and aluminum seal. The glass jar was also purged with nitrogen before closing with a Teflon lined plastic screw cap.

Irradiation: The specimen vials were irradiated at ambient temperature using the Cesium ^{137} radiator or electron-beam accelerator in a range of 5-50 kGy. The dose rate of the Cesium source has been established by using National Institute of Standards and Technology dosimeters and is approximately 0.1 kGy/min. The radiation dose absorbed/received by the tested specimens was measured by a dosimeter made of alanine (Brucker Instruments, Inc., Billerica, MA) or FW-60 radiochromic film (Far West Technology, Inc., Goleta, CA) according to the ASTM E1275 method. The unirradiated and irradiated specimen vials and jars were stored in a refrigerator before subsequent analyses.

Analytical methods: Volatile compounds present in the test materials were analyzed by using headspace GC/FID and GC/MSD, and/or thermal desorption (Komolprasert et. al, 1999). Nonvolatile compounds were extracted from the test specimen with a food simulating solvent (Adhikari et. al., 1997) or an appropriate solvent and quantified by percent soluble solid (Komolprasert et. al., 1999). The nonvolatiles were extracted from the soaker pad specimens using an aqueous 10% ethanol solution and 2-propanol solvent at 40°C up to

10 days. The nonvolatiles were extracted from the PET with boiling methylene chloride or the 10% ethanol solution and n-heptane solvent at 40°C up to 10 days.

Initial Results

Soaker Pad: The results obtained from the HS/GC/MSD analysis at 90»C showed that the 7-kGy gamma irradiation generated 2.3-3.14 ppm 1,3 di-tert-butyl benzene, 0.78-1.40 ppm nonanal, and 0.24-0.41 ppm cyclopentanone. The 1,3 di-tert-butyl benzene is a degradation product of BHT antioxidant used in LDPE layer for soaker pad fabrication. Irradiation significantly increased percent soluble solids extracted from the soaker pad specimens. After irradiation the soluble solid in the 10% aqueous ethanol solution was 0.43 % compared to 0.28% before irradiation. The percent solid extracted from soaker pad specimens using 2-propanol increased with storage time, ranging from 0.7 1 to 0.94 % in unirradiated and from 0.82 to 0.98 % in irradiated. Glucose and cellobiose that were generated from cellulose were present in the soluble solid extracted from unirradiated and irradiated soaker pad specimens with 10% ethanol solution at concentrations lower than 10 ppb based on soaker pad weight. The complete analysis of the soluble solid is underway.

Semi-rigid Crystalline and Oriented PET: The qualitative results obtained from HS/GC/MSD analysis performed at 106°C showed that the 25 kGy gamma irradiation generated 668-742 ppb formic acid, 868-922 ppb acetic acid, 17-32 ppb 1,3-dioxolane, and 47-71 ppb methyl-dioxolane based on PET weight of PET #1 and 2. The results obtained from the thermal desorption performed at 200°C showed that irradiation generated 10-12 ppm acetaldehyde, 479-975 ppb 1,3-dioxolane, and 6.6-10.6 ppm methyl-dioxolane (Komolprasert et. al, 1999). The concentrations of the two dioxolanes found from thermal desorption were much higher than those observed in the HS, although formic and acetic acids were not detected. It is possible that the formic and acetic acids produced by irradiation underwent further reactions with ethylene glycol during thermal desorption to form the dioxolanes.

The soluble solid extracted from various PET specimens before and after irradiation were in a range of 0.67-0.78%. PET cyclic trimer is the major component and is present at 0.41-0.50%, accounting for more than 50% of the percent total solid in PET (Komolprasert et. al, 1999). Statistically, irradiation did not increase the soluble solid and cyclic trimer.

The overall results suggest that 25-kGY irradiation had a slight effect on increasing the volatile but not the nonvolatile compounds detected in the PET specimens.

Semi-rigid Amorphous and Nonoriented PET: The PET materials have been irradiated with electron-beam accelerator at ambient temperature at 5, 25 and 50 kGy. The volatiles are being analyzed using HS/GC/FID and HS/GC/MSD. Nonvolatiles have been extracted using 10% ethanol and n-heptane food simulating solvents. Irradiation did not increase the percent soluble solid. Regardless of irradiation, soluble solid extracted from the PET using both food simulants is lower than 0.02% based on the PET weight.

References

Adhikari, C, Komolprasert, V., and Thayer, D.W., 1997. Effects of gamma irradiation on soaker pads in the presence of an aqueous food simulant. Poster presented at the annual IFT meeting, June 17, Orlando,FL.

AOAC, 1990. Official Methods of Analysis of the Association of Analytical Chemists, Williams, S. (Editor), 15th Ed. Association of Official Analytical Chemists, Inc. Arlington, VA.

FDA, 1992. "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations." Chemistry Review Branch, U.S. Food and Drug Administration, Indirect Additives Branch, HFS-247, 200 C Street, S.W., Washington, DC 20204.

FDA, 1993a. "Recommendations for Chemistry for Indirect Food Additives Petition." Chemistry Review Branch, U.S. Food and Drug Administration, Indirect Additives Branch, HFS-247, 200 C Street, S.W., Washington, DC 20204.

FDA, 1993b. "Food Additives: Threshold of Regulation for Substances Used in Food-Contact Articles," Proposed Rules, Federal Register, Vol. 58, No. 195, pp. 52719-52726.

FDA, 1995a. "Food Additives: Threshold of Regulation for Substances Used in Food-Contact Articles," Final Rule, Federal Register, Vol. 60, No. 136, pp. 36582-36594.

FDA, 1995b. "Recommendation for chemistry data for indirect food additive petitions." Chemistry Review Branch, HFS-247, U.S. Food and Drug Administration, Washington, DC 20204.

FDA, 1997. "Irradiation in the Production, Processing and Handling of Food, Final Rule, Federal Register, volume 62, No. 232, pp. 64107-64121.Komolprasert, V., Armstrong, D. and Hargraves, WA, 1994. Determination of benzene in recycled polyethylene terephthalate (PET) by dynamic purge and trap headspace gas chromatograph (HS/GC). Food Add. Contam. ll(5): 605-614.

Komolprasert, V., and Lawson, A, 1994. Effects of aqueous-based washing on removal of hydrocarbons from recycled polyethylene terephthalate (PET). Proceedings for the ANTEC?94 conferences of Plastics Engineering, Society of Plastics Engineers (SPE), Vol. Ill: 2906-2909.

Komolprasert, V., Lawson, A.R., and Hargraves, W.A, 1995. Analytical method for quantifying butyric acid, malathion and diazinon in recycled polyethylene terephthalate). J. Agric. Food Chem. 43(8): 1963-1965.

Komolprasert, V. and Lawson, A., 1995. "Residual Contaminants in Recycled Poly (ethylene terephthalate)-Effects of Washing and Drying," in Plastics, Rubber, and Paper Recycling: A Pragmatic Approach, ACS Symposium Series 609, C.P. Rader, S.D. Baldwin, D.D. Cornell, G.D. Sadler and R.F. Stokel (editors), pp. 435-444.

Komolprasert, V. and Lawson, A., 1997. Considerations for reuse of polyethylene terephthalate) bottles in food packaging: Migration study. J. Agric. Food Chem. 45(2): 444-448.

Komolprasert, V., Lawson, A. and Begley, T., 1997. Migration of residual contaminants from secondary recycled poly(ethylene terephthalate) into food simulating solvents, aqueous ethanol and heptane. J. Food Additives and Contaminants. 14(5):491-498.

Komolprasert, V., Lawson, A. and Gregor, A., 1996. Removal of contaminants from RPET by extrusion remelting. J. Packaging Technology and Engineering, September, pp. 25-31.

Komolprasert, V., McNeal, T., Agrawal, A., Adhikari, C. and Thayer, D.W., 1999. Volatile and nonvolatile compounds in semi- rigid polyethylene terephthalate after 25-kGy gamma irradiation. Poster prepared for the annual IFT meeting, July 25, Chicago, IL

J. Pack.Sci. Tech. Vol.8 No.6 (1999)

Review

Influence of the European and German Environment Legislation on the Food Packaging Tecknology in Germany

Horst Weisser*

An overview is given about the European and German Environment Legislation on the Food Packaging Technology in Germany. The following aspects are treated: Laws and regulations, DSD - Dual System Germany, methods for the recycling of used plastic bottles, life cycle assessment, reusable or refillable packaging, inspection of refillable bottles (empty bottle inspection machines, sniffers for plastic bottles). Finally a report is given on our own research about scuffing of glass bottles and the usability of pet bottles for beer.

Keywords: Packaging legislation, Green Dot, recycling of plastic and plastic bottles, life cycle assessment, PET-recyclat, challenge-test, returnable or reusable packaging, sniffer, scuffing of glass bottles, PET-bottles for beer, ageing of beer, beer flavour stability

1 Packaging Consumption and Recycling in Germany

The enthusiasm of German consumers for the separate collection of recyclable waste is unflagging. In 1998 they collected a total of 5,622,525 t of used sales packaging manufactured from glass, paper, cardboard, plastics, tinplate, aluminium and composites in the Green Dot collection containers. This even exceeded the high result of 5,618,445 t which was achieved in the previous year. Including impurities, 6,215,416 t (1997: 6,051,250 t) were collected by way of the Dual System Germany[1]. This corresponds to a per capita collection of 75.8 kg (1997: 73.7 kg). The recycling and recovery requirements prescribed by the Packaging Ordinance were achieved for all material fractions (**Table 1**).

With this result, the German public has once again proved by its actions that it considers packaging recycling to be a good thing for the environment. This opinion which is also documented by life cycle analyses is reflected in a study published by the *Gesellschaftfur Konsumforschung* (*GfK*) in March 1999[2]. According to this, almost eight out often people questioned (77%) consider collection and recycling to be the best concept for the disposal of waste. Not even every fifth person (17%) is in favour of waste incineration, and only four percent are for landfilling.

Table 1 *Recycling of used packaging in 1998 in Germany (DSD)*

	Licensed quantity in t	Recycled quantity in t
Glass	2,965,595	2,704,859
Paper/cardboard	843,059	1,415,502
Plastics	516,879	600,015
Composites	575,879	34,962
Tinplate	324,947	374,873
Aluminium	37,458	43,343
Total	**5,263,425**	**5,483,554**

Institute for Brewery Installations and Food Packaging Technology, Technical University of Munich, D-85350 Freising-Weihenstephan, Germany

2 Laws and Regulations

Several ***laws and regulations*** were ratified within the *European Community (EC)* and *Germany* to reduce the amount of packaging waste. The most important regulations for the packaging industry and the consumers are:

- European Parliament and Council Directive 94/62/EC of 20 December 1994 on Packaging and Packaging Waste
- German Waste Avoidance, Recycling and Disposal Act (Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG) of 7 October 1996
- German Packaging Directive (Verpackungsverordnung - VerpackV) of 21 August 1998 (Regulations on the avoidance of packaging disposal).

The cornerstones of the new legislation are: consistent application of the *Polluter Pays Principle*, creation of a prevention-oriented hierarchy of obligations (*avoidance before thermal or material recycling*), equal status of thermal and material recycling, with the possibility of determining a priority in the case of specific waste forms by statutory order and producers' responsibility for their products (to be reified in each case by statutory order).

2. 1 EU Directive 94/62/EC

It can be assumed that everyone with a commercial interest in packaging is aware of the ***European Parliament and Council Directive 94/62/EC on Packaging and Packaging Waste***[3]. But probably few people realise that it is not purely about environmental protection. Indeed, the purpose of the Directive was to complete the single European market and this was the legal basis of its adoption late in 1994 by the then 12 EU member states

Directive 94/62/EC aims to harmonise the national packaging legislation with the twin objectives on the one hand of preventing or reducing the environmental impact caused by packaging and packaging waste and on the other hand, ensuring the functioning of the Internal Market in a manner that the obstacles to trade and distortion and restrictions of competition can be avoided.

The Directive contains a list of *must* do and *may do items* for member states. The major risk of market disruption results from the *may do list*. Examples include: member state mandatory quotas for reusable packaging; packaging Eco-Taxes; product specific targets for recovery and or recycling; bans on packaging which meet European law essential requirements; some labelling and marking requirements and national products standards for packaging.

Undoubtedly the most controversial and misunderstood of all these are reuse quotas. The Directive says *"member states may encourage reuse systems of packaging, which can be used in an environmentally sound manner, in conformity with the Treaty"*. Quotas for reusable packaging contained in the 1991 German Packaging Ordinance are presently the subject of an infringement action by the European Commission. The Commission claims these quotas infringe Article 30 of the Treaty which prohibits quantitative restrictions on imports and all measures having equivalent effect. Brussels contends that the imposition of high reuse quotas for various types of beverages sold in Germany puts foreign companies at a competitive disadvantage and is therefore a trade barrier.

2.2 German Waste Avoidance, Recycling and Disposal Act

In 1 993, the German federal government decided to reformulate *Waste Disposal Act (Abfall-Beseitigungsgesetz, AbfG)* on 1 0.06.72 into a ***Waste Avoidance, Recycling and Disposal Act*** *(Kreislaufwirtschafts- und Abfallgesetz - KrW-/AbfG)*[4]. The aim was to realise the economically viable recycling of materials within an environmental and social market economy. The new, reformulated Act came into force on 07.10.96. With it, a new, *preventive concept of waste* has been created. According to this concept, waste is no longer simply something that the owner wishes to be rid of, but also those substances, surpluses and residues, which are neither deliberately produced nor used for any purpose. These include, for example, swarf or harmful industrial substances as well as scrap cars or waste paper. The new waste concept, taken from European law, is now also applied at national level.

The main goal of the new Act is to develop waste law and waste management towards a recycling economy. The cornerstones of the new legislation are:

- consistent application of the Polluter Pays Principle
- the creation of a prevention-oriented hierarchy of obligations (avoidance before thermal or material recycling)
- the equal status of thermal and material recycling, with the possibility of determining a priority in the case of specific waste forms by statutory order
- producers' responsibility for their products (to be reified in each case by statutory order) extending the opportunities for the privatisation of waste disposal.

Through integrated recycling of functional and auxiliary substances, such as solvents and oils for example, waste is to be avoided as far as possible even at the production stage. On the other hand, the producers' responsibility for their products which is now embodied in law should guarantee that products are structured in a manner that waste is avoided in their manufacture and use, and that an environmentally sound recycling and disposal is ensured after their use.

In addition, *unavoidable waste must be recycled in an environmentally acceptable way*. In this, both thermal and material recycling are equally permissible. In an individual case, the most environmentally sound manner of recycling has priority. The federal government is authorised to lay down the most environmentally sound manner of recycling for individual waste forms through statutory orders. Thermal recycling is nonetheless only permissible where: the waste has a calorific value of at least 1 1,000 kJ/ kg, the furnace operates at as a minimum 75% thermal efficiency, and the heat gained is used by the recycler or delivered to third parties.

Only those waste forms which cannot be recycled may be disposed of. With its strict requests, the Act establishes a very high standard for the environmentally appropriate treatment and storage of the waste to be disposed of.

2.3 German Packaging Ordinance

The aim of the Ordinance[5] is to encourage the avoidance and recycling of packaging waste. Among other things, it stipulates that transport packaging, secondary packaging and sales packaging must be taken back and recycled, prescribes recycling quotas and expressly states that refillable systems must be protected and expanded. Instead of a recycling quota, the original version of the Packaging Ordinance of 1991 contained collection and sorting quotas.

The purpose of the Ordinance is to achieve a drastic reduction in the amount of packaging waste deposited on land fill sites and to organise a closed cycle for recyclable materials with a view to promoting the conservation of resources.

The intention to give the Packaging Ordinance of 1991 a comprehensive overhaul was voiced as far back as 1993. After several subject specialists had put forward their draft proposals, the first draft amendment drawn up by the Federal Government failed to be accepted by the Bundesrat in April 1997. On the basis of the reading in the Bundesrat, the rejected draft was then re-edited and additions were made to incorporate major demands from the federal states. Following an initial phase of intense political debate, a new draft was submitted by the Federal Government and was this time passed by the Bundesrat in May 1998, thus enabling the Packaging Ordinance Amendment to enter into force on 28 August 1998.

The amendments made to the Packaging Ordinance of 1991 predominantly lie in the following areas:

1) Those manufacturers and distributors, who do not want to join an established Dual System, must also in the future submit documentary evidence to show that they have fulfilled the recycling quotas, thus ensuring that all manufacturers and distributors subject to the Ordinance compete on an equal footing.
2) The main steps taken to promote competition within the waste disposal industry include to make the Dual Systems responsible for organising waste disposal services - in the form of collection, sorting and recycling - and demanding that all packaging collected are forwarded for recycling under competitive conditions and that waste disposal companies make known the costs they incur for recycling individual packaging materials. In addition, the basic conditions underlying competition between the different systems for different waste management sectors are improved as the quotas to be met are determined in accordance with the volume of packaging licensed by a system.
3) Packaging for products which contain hazardous substances has been incorporated into the area of packaging covered by the Ordinance for the first time. Thus, these regulations have been brought into line with the scope of validity of the EU Packaging Directive.
4) The recycling quotas stipulated have been revised on the basis of the principles of the *new Product Recycling and Waste Management Act* (KrW-/AbfG). The ambitious figures laid down should be maintained. An appropriate network of facilities should be set up for the purpose of achieving these quotas on a staggered basis over a period of time and should reach completion during 1999.
5) The intended amendment continues to regard refillable beverage packaging as an ecologically advantageous type of packaging and treats it appropriately.

Collection and Sorting Quotas

The first version of the Packaging Ordinance (valid from 1991 to 1998) prescribed deadlines and quotas for all packaging materials for the collection and sorting of post-consumer sales packaging. To confirm that it was meeting the quotas for the collection, sorting and recycling of the collected sales packaging, the *Dual System* submitted proof in the form of mass flow verifications to the Ministries for the Environment of the individual federal states of Germany.

The quotas were continually increased until 1995, when the collection quota for all packaging materials was 80 percent, 80 to 90 percent of which had to be sorted. The collection and sorting quotas were abolished when the Packaging Ordinance Amendment came into force and now only a recycling quota remains.

Refillable systems

Refillable systems have a substance cycle already in use, predominantly for glass and sometimes PET packaging. For example, consumers are demanded to pay a deposit on beverage bottles or yoghurt jars which is refunded when the consumer brings the empty bottles and jars back to the retailer.

The Dual System is committed to maintain and expand refillables systems which have proven successful to date. Under the Packaging Ordinance, the German beverage industry is obliged to meet a nation-wide refillables quota of at least 72 percent. As can be seen in Table 2 this is not reached since 1997. In these days a heavy discussion is going on what the Federal Government will require in the future.

Table 2 *The proportion of refillables in the beverage sector in Germany in %*

Beverage sector	*1991*	*1992*	*1993*	*1994*	*1995*	*1996*	*1997*
All beverages (excluding milk) Error margin: max. 1%	71.69	73.54	73.55	72.87	72.27	72.21	71.35
Mineral water	91.33	90.25	90.89	89.53	89.03	88.68	88.32
Fruit juices and other non-carbonated drinks	34.56	38.98	39.57	38.76	38.24	37.93	36.65
Carbonated soft drinks	73.72	76.54	76.67	76.66	75.31	77.50	77.54
Beer	82.16	82.37	82.25	81.03	79.07	79.02	78.00
Wine	28.63	26.37	28.90	28.54	30.42	28.66	28.55
Milk in refillable packaging	24.17	26.80	26.56	24.69	22.54	20.10	17.99
Milk in a tubular bag	2.10	1.53	1.41	2.25	5.90	10.50	12.22

3 Duales System Deutschland – DSD

In Germany a second (dual) waste management system for post-consumer sales packaging is supplementing the existing public waste disposal service. Its legal base is the Packaging Ordinance. The Dual System is a privately organised system for the collection and sorting of used packaging and it is operated by *Duales System Deutschland AG*, or DSD, a non-profit organisation based in Cologne. It generates funding by charging licence fees for the use of the Green Dot symbol.

3.1 Green Dot

The green Dot is a registered trademark of DSD being used to identify sales packaging which can be recycled if it is fed back into the Dual System's collection systems. Manufacturers, fillers and importers pay a licence fee which entitles them to have their *Green Dot* packaging disposed of by the Dual System.

Austria. France, Belgium, Luxembourg, Spain, Portugal and Ireland have also set up (or are in the process of setting up) systems based on the model of the Dual System.

The DSD sets up collection systems close to consumers' homes and takes back used sales packaging in accordance with the specifications of the Packaging Ordinance, thus exempting retailers and manufacturers from their individual take-back obligations.

The DSD is monitored by the environment ministers in Germany's federal states to ensure that the collection and sorting quotas are met. Records of performance of the Dual System are produced in the form of mass flow verifications.

Licence fees for the Green Dot

The Green Dot fee consists of a weight fee per material and an item fee. The item fee is calculated either according to the volume or area of a piece of packaging (**Figure 1)**.

In general, one item fee is charged for each piece of packaging (see Example **Table 3**). If individually wrapped articles are packed together in a multipack, several item fees will be charged accordingly.

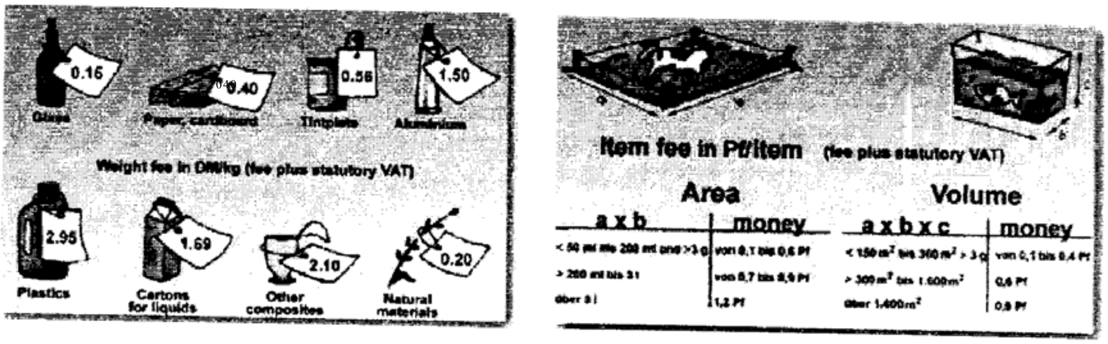

Figure 1 W*eight fee in DM/kg and Item fee in Pf/Item Packaging Material for the Green Dot*

Table 3 *Example: 250 g plastic yoghurt tub with aluminium lid*

Plastic tub,6.62g×2.95DM/kg	1.95Pf
Aluminium lid,0.51g×1.50DM/kg	0.08Pf
Total weight fee	2.03Pf
Volume category V6(200-400ml)	0.70Pf
Total licence fee	2.73Pf
Minus a reduction of 9.5% from 01.01.1991 on	2.47Pf

3.2 Green Dot - Society for System Technology

In 1997 DSD has set up its subsidiary company *Green Dot - Society for System Technology (Der Grüne Punkt-Gesellschaft für Systemtechnologie mbH)*, for pushing forward the process of developing efficient sorting processmg and recycling techniques. The company's amassed expertise will help to reduce the Dual System's waste disposal costs and to improve further the quality of the sorting process and the materials used for recycling

Tasks are:

- Promoting the development of sorting, processing and recycling technologies
- International sale of German sorting, processing and recycling technologies.

The project with Japanese company *Hitachi Ltd.* is progressing very well. In 1997, the Hitachi group purchased the rights to a processing system for mixed plastic waste and now intends processing mixed plastic packaging in a plant in Kita-Kyushu, Japan, before being used as a substitute for heavy oil in the reduction of iron or in blast furnaces[6].

3.3 German Society for Recycling Plastic Material - DGK

The *German Society for Recycling Plastic Material (Deutsche Gesellschaft für Kunststoff-Recycling mbH - DGK)* is guarantor for the proper recycling of used plastic sales packaging marked with the Green Dot Before the plastics collected through the Dual System can be recycled, they have to be sorted and, in some cases, processed ready for recycling.

The Dual System sorting plants currently sort plastics into the following five fractions: *Films* such as plastic bags make up 26% of the total. *Bottles*, for example for shampoo or washing-up liquid, account for 9% *Cups* and *Tubs* - most of them used for dairy products - and expanded polystyrene (EPS) together account for 2% All these materials are high-quality plastics (PP, PE or PS) suitable for processing into regranulate. The largest share of the sorted plastics is mixed plastics (around 63%). These are mostly small items and packages composed of different materials, or packaging components which cannot be economically separated. They are pressed into bales and processed in special processing plants to produce a homogenous, pourable bulk material or agglomerate. This is usually recycled as a feedstock.

3. 3. 1 Methods of Plastic Recycling

Mechanical recycling: Mechanical recycling involves shredding, melting down and re-forming sorted packaging, so the new plastic products are made of the same materials as the original products.

Feedstock recycling: With feedstock methods, the plastics are broken down into their constituent oils and gases. Some sorting is required before this can take place, although it is just a matter of ridding the plastics of any pieces of metal or foreign matter.

3. 3. 2 Recycling of the Mixed Fraction

More than 60% of the sales packaging collected by the Dual System are heterogeneous and contaminated small-sized plastics. As further sorting into pure plastic fractions would make little economical sense, these plastics are separated as the so-called mixed fraction. Pressed into bales they arrive at the preparation plant, where they are prepared for feed-stock recycling

Every feedstock preparation process starts with a shredding step: The plastics are processed into a homogeneous material with a particle size of less than 50 mm which is easy to handle in subsequent preparation steps.

After the plastics have been coarsely shredded, *impurities* and household waste items which have not been separated in the sorting plant *have to be removed*. Removing these impurities improves the processability of the material significantly and protects the machinery from excessive wear and damage. Magnetic separators are used to isolate ferrous metals. Eddy-current devices handle the separation of non-ferrous metals such as aluminium. Air separators and sieves are used to remove other impurities.

Compacting the material is an essential step in the preparation process. Three equipment alternatives are available: agglomerators, pelletisers and disc compactors. In a disc compactor, the shredded plastics are compressed and plastified using high friction. The result of the compacting should be a homogeneous pourable bulk material with a particle size of about 10 mm. Oversized granules are ground down or sieved out.

The *output product* of the preparation process is a mixed plastics agglomerate with a high density, a defined particle size, a low chlorine content and little residual moisture. It can be used in all feed-stock recycling processes.

- In the hydrogenation process, the material is converted into synthetic crude oil (syncrude).
- The pyrolysis technique developed by BASF cracks the plastics into their basic chemical components.
- And steel companies use the agglomerate as a reduction agent in their blast furnaces.

3. 3. 3 Examples of Feed-stock Recycling Processes

Methanol production: The *SVZ (Sekundärrohstoff- Verwertungszentrum Schwarze Pumpe)* recovers synthesis gas from plastic waste. This primarily contains carbon monoxide and hydrogen and is a starting product for chemical syntheses. The SVZ uses it to produce methanol which for instance is required to produce plastics or adhesives.

PARAK process: A feedstock recycling process for plastic waste (only PE and PP) with a mechanical component. With the aid of this method, the *Paraffinwerk Webau GmbH* recovers oils and paraffin from plastics. Paraffin can be used universally, for instance as corrosion protection agent, wax, polish, the basis for creams etc.

Reduction process: *Stahlwerke Bremen* use a blast furnace process for the production of steel. The process is in principle a technique to produce pig iron for the steel industry. Plastics in the form of agglomerate are used here in a I : I relation as a substitute for heavy oil, a reducing agent that is used to remove oxygen from the iron.

Gasification process: *SVZ (Sekundärrohsloff-Verwertungszentrum Schwarze Pumpe)* has developed a high pressure gasification and Rheinbraun a high temperature W*inkler process* for gasification.

Hydrogenation: A feedstock recycling process implemented in the *Kohleöl-Anlage Bottrop of VEBA AG.* The main product is a high-grade synthetic crude oil, syncrude, which can be used as feedstock tor the production of plastics, gasoline, diesel fuel and heating oil. 800 kg of syncrude can be recovered from one tonne of mixed plastics. These days it was decided that due to uneconomicalness the plant will be closed at the end of this year!

Cracking: *BASF, Ludwigshafen* has stopped the pilot plant on cracking of plastic feedstock.

4 Methods for the recycling of used plastic bottles

Different methods exist for the recycling of used plastic bottles. In the new developed process of OHL Company[7] the recovered flakes from other recycling methods are extruded, recondensated and granulated in a specially built extruder to transform recovered flakes into an acetaldehyde-free product for 100% reuse in the plastic bottle cycle. During the process, acetaldehyde, oligomers and all contaminants are eliminated, thus ensuring the pellets are totally suitable for contact with beverages or food.

Schmalbach-Lubeca[8] acquired the rights to the Supercycle® process when it took over the PET operations of *Johnson Controls*. The food-grade Supercycle material is produced by a proprietary cleaning process which works so thoroughly that the recycled PET material and the bottles produced from it are completely free of any contamination. This fact is confirmed by leading food-industry institutes in Europe as well as by the Food and Drug Administration in the USA, which has the strictest standards in the world. Schmalbach-Lubeca operates two plants that recycle used PET containers by the Supercycle process: one in Novi, Michigan/USA, and since the end of 1997 one in Beaune, France.

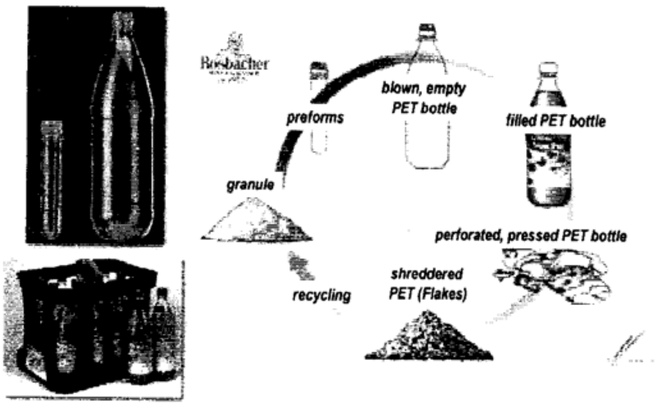

Figure 2 Example ofa Supercycle PET Bottle, Rosbacher Mineralbrunner[9]

4. 1 PET Recyclate for Direct Contact with Foodstuffs

For monitoring and sorting out contaminated plastic refillable bottles, a so-called *sniffer* is currently used as standard on a bottle washing line. The application of this together with tests for the cleanliness, shape and solidity (no leaks) of the bottles already guarantees a high degree of safety. There is however no information about the chemical inertness of the refilled plastic bottles. This knowledge is indispensable for carrying out quality controls in industry and for testing bottles already in the marketplace regarding their suitability for consumables. The test also provides the basis for further material developments and economic improvements.

The *Fraunhofer Institute for Process Engineering and Packaging (1VV) in Freising* determined the present *is-state* of PET recyclates, namely the levels of the relevant migratory impurities, and also evaluated analytical methods for quality assurance. In addition, about 150 PET samples from 14 European recycling companies and PET recyclate users were examined over a long time period. On top of that, the researchers quantified the amounts of acetaldehyde and limes which were present in all samples.

The samples were analysed using the following three different analytical methods:
- gas chromatography headspace analysis,
- high speed extraction followed by gas chromatography and
- polymer extraction followed by gas chromatography.

The most suitable analytical method for quality assurance proved to be gas chromatography headspace analysis. Using this method, even the smallest amounts of relevant migratory substances in the PET material could be reliably detected. Compared to the two extraction methods, headspace analysis requires no sample preparation. This simplifies the method and also considerably reduces the costs and time required. The new analytical method for quality assurance enables the operators of PET recycling plants to routinely monitor their recycling process. The system is very robust and simple to operate. Within a few hours it provides data about the purity of the PET recyclate. Using this knowledge about possible contaminants and their concentration levels, the existing PET recycling processes can be optimised.

4. 2 Challenge-Tests for the Testing of the Cleaning Efficiency of Different Recycling Processes

Due to modern environmental packaging requirements the *recyclability of post-consumer PET-recyclate* into new food packaging applications is of increasing importance[10]. The recycling process and the quality assurance of the PET-recyclate must satisfy special requirements. The *Fraunhofer Institute IVV* has developed *challenge-tests* for testing the cleaning efficiency of different recycling processes. These Challenge-Tests investigate if a recycler provides a PET-recyclate quality suitable for direct contact applications. For challenging a PET-recycling process for post-consumer soft-drink bottles post-consumer PET flakes are artificially contaminated with model contaminants or so called surrogates. In worst case scenarios misuse of PET-beverage bottles such as storage of domestic chemicals and the possible introduction of these compounds into the recycling process is simulated.

The surrogates are chemical substances with different chemical structures and different physical properties. They are chosen such that they represent the four general categories of chemical compounds: volatile and non-polar, volatile and polar, non-volatile and non-polar, non-volatile and polar. In addition a wide range of functional groups is used in order to reflect the different chemical and physical properties of real-life contaminants. In contrast to FDA procedure IVV use no excessive solvents for the surrogates. Therefore the amount of contaminated waste is reduced and makes this Challenge-Test more user-friendly and economical.

Within the standards, measurements & testing programme (SMT4-CT96-2 129) *Establishment of a standard test procedure for refillable PET bottles with respect to chemical inertness behaviour as well as sensory interactivity including preparation of a certified reference PET material* one reduced set of model compounds (consisting of propylene glycol, phenol, menthol, benzophenone, toluene, p-xylene, limonene and phenylcyclohexane) was tested[11].

4. 3 Fair Project Recyclability[12]

Food packaging regulations in Europe require that the packaging materials must not cause mass transfer (migration) of harmful substances to the food. Considerable scientific progress has been made in understanding and modelling the diffusion and migration of adventitious hazardous substances from recycled plastics into foodstuffs in direct or indirect contact with the food. Most of this knowledge has been elaborated within the recently finished EU project AIR-CT93-I014[13]. One of the main conclusions of this project was that PET is a low diffusivity plastic and is the most promising polymer for reuse as a food packaging material. Furthermore, from the project's results and taking the existing FDA's position into account, for the first time in Europe an attempt has been made within an *International Life Sciences Institute* (ILS1 Europe) expert group to draft corresponding guidelines and recommendations for the safe reuse of plastics for food packaging.

Nevertheless, the practical translation of this progress into innovative industrial solutions is still awaited One of the reasons has typical *European* character and can be substantiated by the fact that the European legal requirements in this respect are not yet clearly and uniformly defined. As a consequence, the second reason is the lack of economic and generally recognised test methods.

With respect to PET, although being the most promising candidate plastic for recycling, there is clearly an obvious reason for the industrial hesitation in launching advanced food packaging applications. In the whole chain of knowledge on diffusion and migration into and out of PET - which allows for instance to correlate a known initial concentration in the plastic with the resulting time-dependent concentration in a foodstuff - there remains one missing link: This is the still open but highly important question of the nature and concentration of actual contaminants found in collected PET such as that originating from soft drink bottles. Filling up this gap with analytical data relevant for the whole of Europe, and then linking this statistical picture with the available knowledge on PET diffusion behaviour, would enable to draw scientifically sound and convincing conclusions about the safety of reusing PET. This in turn would allow to derive the appropriate test conditions and methods for industry to use and for recommending to the Commission for future regulations. These methods will offer for the first time the possibility of being not too exaggerated and overchallenging - which is presently necessary as a precaution due to the current lack of knowledge - but being practical and economical whilst safe-guarding the consumer at the same time.

The objectives of the project are:

- To facilitate industrial innovation and to harmonise legislative enforcement of new environmental packaging requirements stemming from the Directive 94/62/EEC on packaging and packaging waste, by
- Drawing up a statistical overview of the nature and extent of contaminants in PET recovered from the food packaging market, in order to establish an evaluation platform for the quality and safety-in-use of recycled PET plastics for food packaging and
- Generating a scientific understanding of the physico-chemical behaviour of chemical contaminants on paper and board fibres as a basis for safety evaluation and definition of criteria for the appropriate reuse of recycled fibres for food packaging.

5 Life Cycle Assessment

The aim of a life cycle assessment is to highlight the negative impact which products have on the environment from the time they are produced right through to the time they are disposed of and to analyse the associated effects of this impact with a view to creating a basis for assessing all types of products. In future, the life cycle assessment will play an increasingly important role in the selection of packaging.

The *Federal Environment Agency of Germany* has had various life cycle assessments drawn up for packaging systems and packaging materials. An initial assessment based on a comparison of recyclable and refillable containers for beer and milk revealed that refillable systems are not fundamentally better than recyclable packaging when longer distances are involved.[14]

For the first time, life cycle assessments have been drawn up with a view to evaluating the methods used for recycling post-consumer plastic packaging. A comparison of the different processes[15] used in plastic recycling has revealed that it is not one specific method, but rather a combination of feedstock recycling and mechanical recycling which is the most ecologically and economically sound solution.

5. 1 Bottles for Mineral Water

GDB (*Genossenschaft Deutscher Brunnen)* has ordered a LCA of PET and glass bottles for mineral water. The Results are:

Refilllable and Recyclable PET bottles[16]: Refillable bottles with 71 g and 25 turns as well as bottles with 56 g and 1 5 turns are significant better than a 50 g bottle with 5 turns. Within the recyclable bottles the Supercycle bottle with 50% recyclate and the multilayer bottle with 40% recyclate are better than usage of PET recyclate in the textile industry.

Refillable PET and Glass Bottles[17]: 0.7-1-GDB and 1 -1-ODB glass bottles with 50 turns are at smaller transport distances of I 10 km superior to the new 1-1-GDB PET bottle. At 180 km there is no significant difference and at longer distances of300 km the PET bottle is ecologically better.

5.2 Vacuum Packed Roast Coffee

The *Fraunhofer Institute for Process Engineering and Packaging IVV in Freising* has presented the results of the first product life cycle assessment for coffee[18,19]. Within the framework of a study, the significant ecological effects of the total life cycle of vacuum packed coffee were investigated. The work was commissioned by Kraft Jacobs Suchard KJS together with the Senate of the free Hanse city Bremen.

The life cycle was balanced right from the cultivation and processing of the *green coffee beans* via the different transport stages, roasting, packaging, wholesale and retail, the shopping journey, preparation for drinking and consumption through to the disposal of the coffee grounds and the packaging.

One of the main points of attention was the comparison of the environmental effects of the packaging with those of the packaged product. We examined the current packagings *Krönung* and *Monobag* at KJS and also a projected variant *Monobag neu*. The effect of different disposal scenarios for the used packagings was likewise taken into account.

The assessment showed some surprising results. For example, it was shown that the transport and logistic processes in the total assessment only contribute to a relatively small degree to the energy consumption and greenhouse effects - although coffee is transported a*bout half way around the world*, namely up to a distance of 19,000 km. Relative to the total life cycle, the packagings which were examined also have little environmental impact. On the other hand, the cultivation and preparation of the coffee, the roasting process, the preparation of the coffee for drinking and the disposal of the coffee grounds all have clear effects.

6 Returnable or Refillable Packaging

Returnable (reusable or refillable) packaging is a type of packaging which, in contrast to one-way (non-renurnable, single trip, disposable) packaging, is cleaned and used again as packaging. In Germany, the discussion on returnabel and one-way packaging still exists because of the increase of cans and PET-bottles for carbonated soft-drinks and mineral water. For different scenarios the above mentioned life cycle assessments were published.

Nevertheless, *efficient returnable packaging systems are as a rule environmentally superior* to the disposable alternatives. A high degree of standardisation can have positive effects: the use of packaging systems from packaging pools, e. g. the NRW-bottle for beer or the GdB-bottle for mineral water, leads to a higher circulation rate, and secondly to the prevention of unnecessary long return journeys being made by empty items.

6. 1 Inspection of Refutable Bottles

To obey the regulations for product liability an empty bottle inspector is required with optimum detection capability for glass bottles (finish, entire threads, inner surface, base, side-wall, scuffed bottles, residual liquid, etc.) and operational safety. So called *sniffers* were used for detecting undesirable foreign substances (e. g. nitrogen compounds, volatile organic compounds, petrochemicals, and hydrocarbons) in empty *plastic bottles*

6. 1. 1 Empty Bottle Inspection Machines

After cleaning bottles must be clean and fit to use. Those bottles not being useable must be detected and removed from the bottle stream before filling. The main faults are:

- bottles with defects, e. g. in the mouth and bottom area, such as cracks, splits, chips, fins, etc.
- bottles containing foreign bodies, mould, pigment or other adhesive residues, metal pieces, plastic films, straws,
- bottles containing residual caustic from the bottle washing machine or other liquids,
- still dirty bottles.

Modem bottle inspectors operate with high speed CCD cameras with integrated analogue-digital converters and very fast picture taking up to 40 µs (1/250,000 s). The inspection units which are nowadays used are: external and interior side-wall inspection, bottom (base) inspection, neck finish (bottle mouth) inspection, thread inspection, metals in bottle, residual liquid detection with infrared inspection (caustic, water, acid, oil) and high frequency radiation (traces of caustic), control of height, diameter, contour, colour, and *especially for PET hollies*, stress cracking, impact scars, leakage, vent slots.

More details can be found in the following publications: COCA-COLA has published *Approval procedures for All* ***S****urface* ***E****mpty* ***B****ottle* ***I****nspectors (ASEBI)* and UNION OF EU SOFT DRINK ASSOCIATIONS (UNESDA) issued *Guidelines for good handling practices of refillable glass bottles*.

6. 1. 2 Scuffing of Glass Bottles

Scuffing is the appearance of wear marks on glass bottles and plays an important role when filling especially carbonated beverages in returnable glass bottles[20,21]. In relation to different laws and standards for product safety (e. g. German Product Liability Law, ISO 9000, HACCP) it is important to know how the scuffing influences the properties of glass bottles. Therefore some strength properties of differently scuffed bottles were tested. On the other hand scuffing is an unwanted appearance for the marketing of high quality products. There were made some investigations on how the bottles become scuffed within the filling plant.

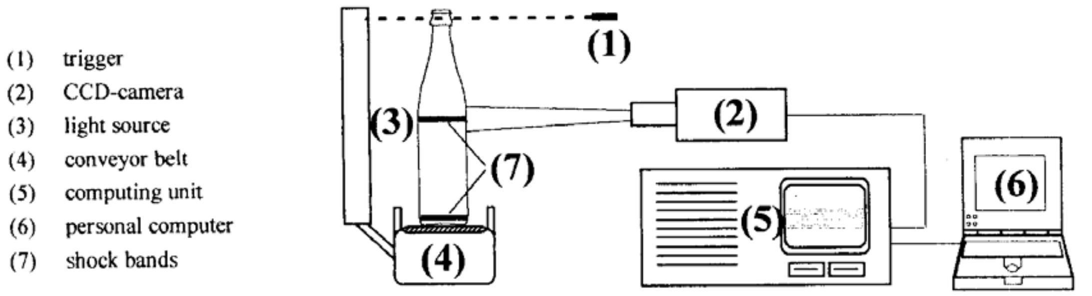

Figure 3 *Scheme of the test rig to detect and evaluate the wear mark area and the degree of Scuffing*

The surface of glass bottles gets mechanically and chemically damaged when passing through bottling lines. During their transport on conveyors or in individual machines within the bottling line the bottles get wear marks (scuffing) or even more severe surface injuries. On conveyors the bottles get mechanically scuffed especially by bottle-to-bottle pressure before glideliners, in combiners, accumulation tables and on the load of the bottle washer and the inlet of the packer. Dirt and water on the glass surface of the bottles accelerates the mechanical damage! In further examinations it could also be shown that the technical standard and the arrangement of the machinery in a filling line as well influence the intensity of scuffing and therefore the theoretical circulation rate. These effects are due to frictional forces between the bottles which are also enhanced with increasing scuffing.

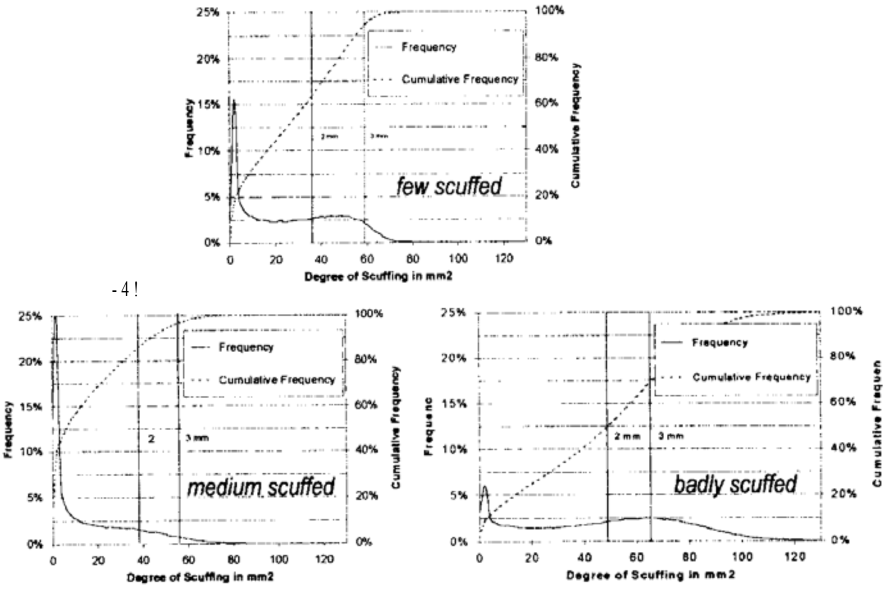

Figure 4 *NRW bottle pool conditions of three German breweries; percentage of bottles exceeding a defined wear mark height*

The bottle surface additionally gets damaged by attacks by chemical action during the washing process. The glass surface is injured and made more sensitive for mechanical stress. Certain detergents like caustic soda, free phosphates, and carbonates attack the surfaces. The effects are influenced by detergent concentration, water hardness, exposure time, and temperature. There are some additives which can reduce the corrosive effect of the lye. But no significant further improvement can be expected because of the required cleaning effect.

The examinations on glass strength related to the degree of scuffing showed that the internal pressure stability and the shock resistance of different shaped returnable glass bottles first decrease with an increasing wear mark height or area. Then a stagnation of stability can be found for both characteristics with increasing degree of scuffing.

The results from this study will help legislators or associations to determine criterions for guidelines and regulations with respect to consumer safety or bottle appearance.

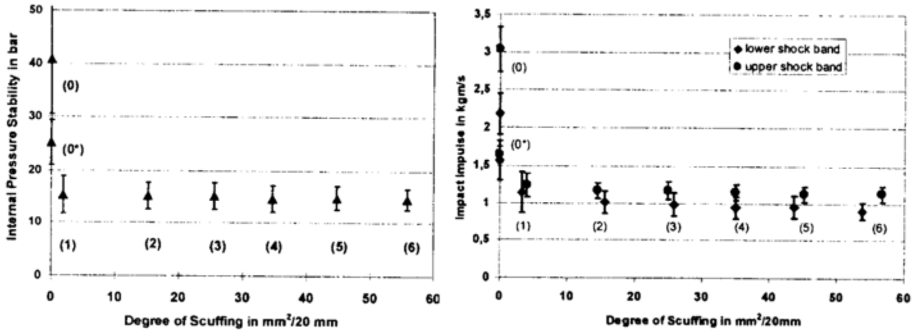

Figure 5 *Influence of the amount of scuffing on the internal pressure stability and the shock Resistance*

PET Bottles Effect of Material Stress - Circulation Rates

The refillable system, with a cycle between bottling plant and consumer, inherently involves the question about the technical suitability and the performance of bottles for beverages, which have been returned, cleaned and refilled. Here, the aspect concerning the chemical inertness of the bottle material against filling with improper substances and in addition the effect of material stress (number of cycles a bottle has been through) can be especially named.

6. 1. 3 Sniffers for Plastic Bottles

Containers for packaging food and bottling beverages have to meet strict European Laws, which means that nobody may be injured or get sick by using it. Returnable bottles have to be exactly inspected before filling[22], especially PET or PEN bottles made of polymer chains which build pores[23]. Therefore plastic bottles are not inert for beverages or other fluids. Some content substances of these fluids e. g. flavours can remain in pores or even migrate further into the plastic material. By cleaning the bottles in the washing machine of a filling plant these substances can remain in the bottle material. The substances may later on migrate back into the bottled beverage.

It is particularly a problem when tilling a sensible beverage like mineral water without a taste in used plastic bottles. The flavours of other beverages can severely influence the taste of the water. Most of the bottlers of mineral water either have individual bottles, or use only new plastic bottles (one-way or returnable only the first time). Some consumers even put other liquids in the plastic containers like oil, fuel or washing detergents.

When using returnable plastic bottles these substances have to be detected and dirty bottles have to be removed. Most of the foreign flavours of before filled beverages or other fluids from the consumers can be inspected by smell or analyse of the residual liquid.

A sniffer has to be placed right after a decapper, often the latter is integrated into the sniffer. It is important to sniff the bottle immediately after decapping because some smells fade away quickly. Most of the sniffers are designed as carousel-machines (rotary-, roundabout-machines). Three or four detection units inspect the gas phase for volatile substances and the remaining fluid phase. A gas sample is taken and analysed in different modules, e. g. by mass spectroscopy sometimes in addition with chemical or electrical ionisation, UV/VIS- and IR-spectroscopy, and measuring the luminescence (fluorescence, phosphorescence, chemoluminescence). The remaining liquid phase is also analysed by spectroscopy methods using the bottle as a test tube by tipping the bottle to one side. The analyses are time extensive but now, up to 50.000 bottles per hour depending on the bottle size can be inspected. A scheme of a sniffer and its inspection modules is shown below.

Most sniffers employ the positive measuring method, which means comparing the measured spectrums of gas and liquid phase with the fingerprints of specific beverage flavours stored in a library. If the detected spectrum is in the positive library, the bottle is accepted. If the spectrum is not known the bottle is rejected. The systems are able to learn new fingerprints by adding them to the library, e. g. when a new product is filled in the plant. The detection methods are not completely reliable, but by using a positive library good results can be achieved.

There could be two or more outlets to split the rejected bottles into groups: e. g. detecting a known flavour of orange to fill a flavoured drink and bottles with unknown spectrums for recycling. Additionally some other inspection modules like testing for leak or geometric distortion could be integrated in a sniffer. The following suppliers are well known: KHS/Grässle, D-Dortmund; Krones/Thermedics Detection, D-Neutraubling; Soudronic, CH-Bergdietikon.

6. 2 PET-bottles for beverages

The use of PET (polyethylene terephthalate) as a material for packaging is increasing all over the world. In the area of refillable bottles for soft drinks, PET is already established as a packaging material due to its properties. Its use is still increasing, especially for the bottling of mineral water. It is expected that new developments such as PEN (polyethylene naphthalenate) will force their way into the beer bottle market in the near future with probable good chances of success.

6. 2. 1 Usability of PET Bottles for Beer

At my chair several investigations has been carried out to study the field *Polyester Bottles for Beer.* We installed a working group with partners of different branches of industry: brewery, bottle and closure producer, chemical industry and filler manufacturer. First aim of the project was to find a *refillable plastic* bottle which is able to guarantee a shelf life of beer of four month at minimum. In the meantime some breweries are filling beer into *one-way bottles*, so our research will be extended to one-way plastic bottles and their properties, too.

Table 4 *Examples of plastic bottles sold in the market*

Carlton brewery, AUS	Coated PET bottle with crown cork, Coating by PPG (Epoxy amine)
Feldschlößchen brewery, CH	Multilayer bottle with two MXD6 barrier liners by Altoplast-Claropac
Karlsberg brewery, D	Multilayer bottle with an EVOH barrier liner by Schmalbach-Lubeca
Heineken breweries, F	Multilayer bottle with oxygen scavenger in the barrier liner, Oxygen scavenger by AMOCO
Miller, USA	Multilayer bottle (5 layers) by Continental PET
Carlsberg brewery, DK	Refillable PEN bottle 38 g by PLM
Bass brewers (Carling), GB	Multilayer bottle with crown cork by Péchiney
De Gayant Brewing Company (Amadeus), F	First sold ACTIS (Amorphous Carbon Treatment on Internal Surface) treated PET bottle by Sidel

At the beginning of the project the influence of the *washing temperature and concentration of cleaning agent (caustic) to the form stability* of the PET bottles which included the measurement of height and volume of the bottles before and past cleaning with caustic solution was examined (Figure 6). In addition, we studied the influence of caustic to the *barrier properties* of PET bottles.

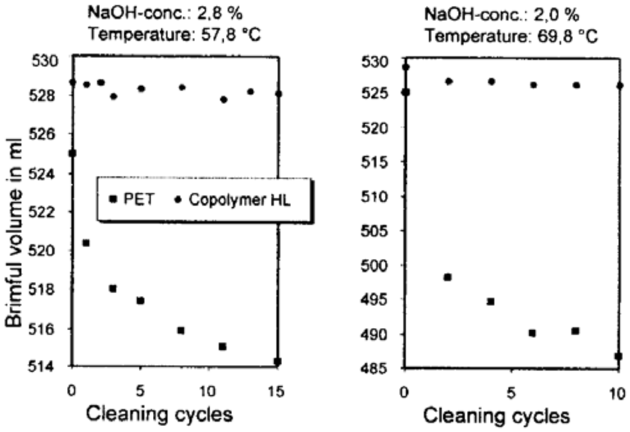

Figure 6 *Influence of cleaning temperature to brimful volume of PET and PET/PEN high level copolymer bottles*

Furthermore investigations were made on the *shelf life of beer in polyester bottles*. Therefore beer was filled into glass bottles (as reference) and into plastic bottles. The applied plastic bottles consisted of 100% PEN. After a storage under different conditions the *ageing components* of the beer were determined by GC-analysis. Also comparative sensory evaluations, so called *tasting of the beer* has been taken place. The aim of these studies was to compare the theoretically, computed shelf life calculate by the results of *permeation measurement* to the real, measured shelf life of the stored beer. The results of these examinations showed that the real oxygen penetration into the plastic bottles differs to the calculated one.

Further a detailed literature survey about the topic *Ageing of beer and beer flavour stability*[24] was appointed. It was purposed to prepare the investigation of the technological possibilities to improve beer flavour stability and their effects on shelf life during storage. Additionally we made some trials in producing beer with different methods of beer stabilisation. Therefore several beers were produced and the flavour stability was examined by analysing the ageing components and tasting the beer.

Ageing components of beer are smell- and flavour-active carbonyl compounds. To measure ageing of beer the sum of ageing-components of beer can be used as a characteristic value. It correlates with the intensity of the tasted ageing-aroma. Ageing components of beer are analysed with a GC-method. The average content of ageing components in fresh beer is about 90 ppm.

Following substances belong to the ageing-components: Succinic acid diethyl ester, 2-methyl-butanal, 3-methyl-Butane$^{*)}$, benzaldehyde$^{*)}$, phenylacetaldehyde, 2-furfural, 5-methy1-2-furfural, γ-nonalactone, phenylethanal$^{*)}$. The$^{*)}$ marked substances can be detected in a higher amount in case of an enhanced oxygen intake in the beer.

During ageing of beer the following changes occur: Loss of palatfulness and of bitterness, changes of aroma profiles. The increase of ageing components correlate with changes in smell and flavour. The flavour impressions are: ribes-flavour, cardboard-flavour, bread or cracker like, caramel or honey like. If beer is extremely old it smells like sherry.

Furthermore we investigated *several bottle types* concerning to their p*ermeation and migration properties* (Figure 7). To study the permeation properties we tested permeation with the MOCON© OxTran O_2-permeation meter. An other method of measuring O_2-permeation was to fill the bottles with degassed water and to measure the permeating O_2 with an DIGOX O_2-meter. During this experiment the filled bottles were stored under different conditions (normal conditions, increased temperature, increased O_2 partial pressure). The intention was to compare the oxygen uptake into the empty bottle and the filled bottle. Additional to this another objective of this experiment was to predict shelf life of defined beer in short term trials. For that purpose we stored beer in the same type of bottle and investigated shelf life by analysing ageing components and tasting. Since the ageing of beer correlates with the O_2-contents of the beer it should be possible to predict shelf life of beer by measuring O_2-increase into the bottle.

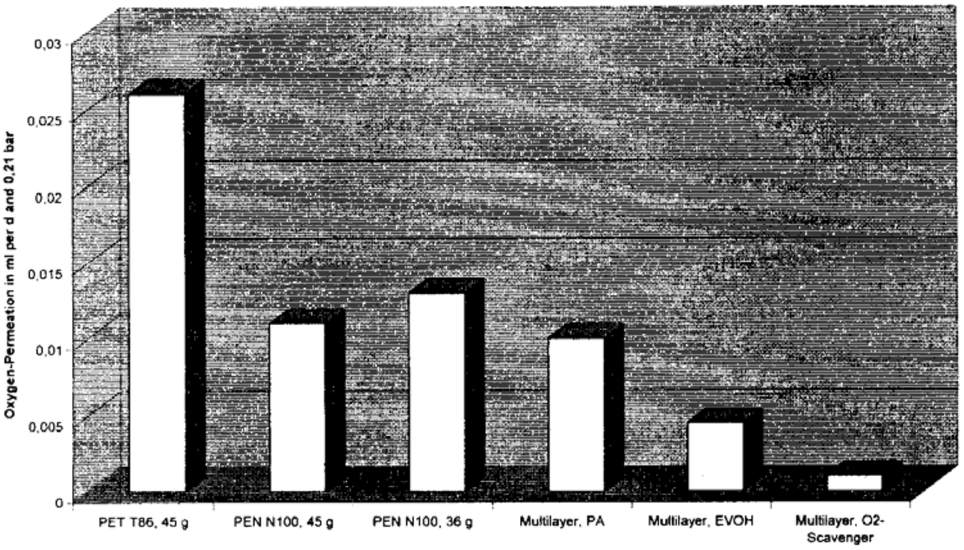

Figure 7 *Oxygen-permeation of different bottle types (Volume 0. 5 liter)*

To achieve a long shelf life of the beer the polyester bottle should have following properties:

- The ingress of oxygen should be very low
- The loss of CO_2 should not increase 10%
- The UV-transmission rate should be very small
- Acetic aldehyde does not influence the taste of beer.

The *migration of aroma compounds and ageing components* was studied with different bottle types. The bottles were cleaned with caustic different times to simulate a varying number of cleaning cycles followed by the filling of the bottles and the storage under various conditions. Past storing the bottles the beer was rejected and the bottles were cleaned another time. Some of the bottles were cleaned again with caustic, the rest of the bottles were cleaned with tap water. The aim of these trials was to show if there is any migration of beer aroma compounds and ageing components of beer into the bottle walls and to test their sensitivity concerning the cleaning with caustic.

6. 2. 2 Future Technologies

Multilayer Bottles with Liquid Crystal Polymers

Superex Polymer, Inc. invented a new multilayer technology[25]. They used Liquid Crystal Polymers (LCP) instead of other barrier liners such as EVOH or MXD6. The advantages of the LCPs are their low costs and high barrier performance. The performance of LCP-PET multilayer is not affected by moisture and it is possible to increase the shelf life of the product at equivalent costs compared to other multilayer solutions. A disadvantage of the LCPs is their opacity. But Superex believes in the possibility to make transparent LCPs in the future.

Interior Coating - ACTIS Plasma Technology by SIDEL[26]

On April 1999 the French Company *Sidel* presented its new ACTIS (Amorphous Carbon Treatment on Internal Surface) process. It endows PET packages with unmatched barrier properties. The company clame to be able to increase the Oxygen barrier properties 30 times compared to traditional, single layer PET bottles, and the CO_2, barrier is supposed to be seven times stronger. Thus the PET bottles' barrier properties would be comparable to glass bottles and metal drink cans.

The process consists of coating the inside of a standard, single layer PET bottle with a layer of highly hydrogenated amorphous carbon, obtained from a food safe gas in its plasma state. This coating creates a thin (about 1/10th micron thick) barrier inside the bottle. Its food safe quality has been approved by TNO in the Netherlands and the treated bottle is 100% recyclable.

Plasma treatment is performed by a machine located downstream from the PET blow-molding machine. Its design is based on *Sidel's* proven rotary, high output rate technology. The first model of this new technique is known as ACTIS 20, and both process and technology are protected by *Sidel* patents. The ACTIS machine is equipped with 20 stations, and treats 10,000 PET bottles per hour for container sizes up to 0.6 1.

Exterior Coating

Amcor & Foster 's Brewing Group sold the worlds first commercial barrier coated beer bottle27. The bottles they used to fill Carlton Cold Filtered beer were 400 ml clear PET bottles with a 50 mm champagne base with external epoxy amine coating by PPG. It is sold as a single serve container but it should be easy to recycle,

7 Literature

1) Duales System Deutschland AG, Köln: http://www.gruener-punkt.de/e/index.htm
2) Gesellkschaft für Konsumforschung (GfK), Nürnberg, 1999: http://www.gfk.cube.net
3) European Parliament and Council Directive 94/62/EC of 20 December 1994 on Packaging and Packaging Waste. Official J. European Communities L365 , 31/12/1994, p. 10-23
4) Waste Avoidance, Recycling and Disposal Act of 27 September, 1994 BGB1 I p 2705 (Kreislaufwirtschafts- und Abfallgesetz – KrWV-AbfG) modified of 7 October 1996, BGB1. I p. 1354
5) Ordinance on the Avoidance and Recovery of Packaging Waste (Packaging Ordinance - *Verpackungsverordnung - VerpackV*) 21 August, 1998, BGB1I, p. 2379
6) http : //www. gruener-punkt. de/e/co ntent/daten/pm99 0708. htm
7) Ohl Apparatebau & Verfahrenstechnik, Limburg: http://www.ecotechnikum.net
8) Schmalbach - Lubeca, Ratingen : http : //www.*Schmalbach. com/investoren/iv_fue_l. him*
9) http://www.rosbacher.com/pet.htm
10) Welle, F.; Franz, R: PET-Recyclate for Food Packaging. In Barrage, A.; Edelmann, X. (Eds..)/EMPA- R'99 Recovery, Recycling, Re-integration. Collected Papers of the R'99 World Congress. Geneva Switzerland February 2-5, 1 999. Volume III: Logistics-Network - Identification and Separation. Mechanical Recycling - Product Design - Eco Design Innovation. St. Gallen: EMPA, 1999, S. 514-517
11) Palzer, G.; Franz, R: Chemische Inertheit von PET-Getränkemehrwegflaschen. Testmethode zur Bestimmung der Inertheit und somit Beschaffenheit des PET-Flaschenmaterials. Kunststoffe 88 (1998) Nr. 6, S. 862-865
12) http://www.ivv.fhg.de/fair/index.html

13) EU-Project AIR2-CT93-1014: Working group 2. Mechanical Recycling (Thermoplastics). Final Report, November 1997

14) German Federal Environmental Agency: http ://www. umweltbundesamt.de/uba-info-e/e-willko.htm

15) Heyde, M.; Kremer, M.: Recycling and Recovery of Plastics from Packagings in Domestic Waste. LCA-Type Analysis of Different Strategies. Bayreuth: Eco-lnforma Press, 1999. ISBN 3-928379-57-7, 194 S. a. appendix (LCA Documents 5)

16) Plinke, E.: Ökologische Bilanzierung von Mehrweg- und Einweg-PET-Flaschen. Der Mineralbrannen 49 (4), 124-129 (1999)

17) Plinke, E.: Ökologische Bilanzierung von PET- und Glasflaschen für Mineralwasser. Der Mineralbrunnen 49 (5), 【7】-174(1999)

18) First life cycle assessment for vacuum packed coffee, http://www.ivv.fhg.de/presse_kaffee_e.html

19) Diers, A.; Langowski, H.-C; Pannkoke, K.; Hop, R.: Produkt-Ökobilanz vakuumverpackter Röstkaffee. Bayreuth: Eco-lnforma Press, 1999. ISBN 3-928379-55-0, 214 S. (LCA Documents 3)

20) Jirikovsky, S.; Weisser, H.: Analysis of bottle scuffing and its effect on resistance to internal pressure. In: "Engineering & Food at ICEF 7". 3 Vol. (Jowitt, R.), Sheffield: Academic Press, Part 2, p. P29-P32 (1997)

21) Jirikovsky, S.; Weisser, H.: Scuffing - Resistance of glass bottles to internal pressure and shock impact. In: "Proceedings of 3rd Karlsruhe Nutrition Symposium European Research towards Safer and Better Food. 18.-20.10.1998. Karlsruhe": Part 2-Posters (Gaukel, V.; Spieß, W.E.L.), Karlsruhe: Bundesforschungsanstalt für Ernährung, p. 426-434 (1998)

22) Hilche, T.; Haux, A.: Sniffer-Einsatz bei der Getränkeabfüllung. Der Mineralbrunnen 45 (9), 324-329 (1995)

23) Krieg, G.: Grundlagen und Notwendigkeit der Fremdstoffinspektion bei Kunststoff-Mehrwegflaschen. Brauindustrie 82 (5), 278-300 (1997)

24) Narziß, L.; Miedaner, H.; Eichhom, P.: Untersuchungen zur Geschmacksstabilität des Bieres. Monatsschrift für Brauwissenschaft 52 (3/4), 49-57 and (5/6), 80-85 (1997)

25) http://www.foster-miller.com/relsuper.htm

26) Sidel, Le Havre, F: http://www.sidel.com/GB_bouree_com.asp?com=GB_280499

27) Mansour, J.: The World's First Commercial Barrier Coated Beer Bottle: A Case History. Proceedings Nova-Pack Americas '99, Schotland Business Research, Inc. (1999)