A study of human exposure to selected phthalates in toys in Sri Lanka

D. P. Uththamawadu[1, 2], R. D. Wijesekera[2] and S. L Rajasingham[1]
[1]SGS Lanka (Pvt) Ltd, Vauxhall Street, Colombo 02
[2]Department of Chemistry, University of Colombo

Abstract

Phthalates are a chemically neutral class of compounds with low water solubility, high fat solubility and low volatility. They are commonly added to polyvinyl chloride (PVC) as plasticizers. However, as they do not chemically bond to PVC, they can leach from the plastic product during or after its life time. They are suspected cancer-causing agents and possible teratogens. In animal studies chronic effects such as decrease in body weight, increase in mortality and a dose related increase in organ weight of liver and kidney are observed. America, European Union and Japan have restricted the use of certain phthalates in toys which are used by children to 0.1% by weight.

In this study the levels of six phthalates [dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), diisononyl phathalate (DINP) and diisodecyl phthalate (DIDP)] were determined in soft and hard toys obtained from shops in the Colombo central market between December 2009 and June 2010. The phthalates were determined using the method specified by the American Society for Testing and Materials (ASTM). The procedure involved soxhlet extraction of the plastic with a 1:1 mixture of dichloromethane: methanol, followed by a clean up using florisil. The quantitative determination was carried out by GC-MS in SIS mode.

Percentage recoveries in the acceptable range of 70% to 120% were obtained in this study. The detection limits obtained were (by weight): BBP, DBP, 0.003%; DEHP, DNOP, 0.002%; DINP, DIDP, 0.004%. These detection limits are 10 times lower than the legal allowable level of 0.1%.

Only two phthalates (DBP and DINP) were detected in the squeeze type toys. They were found in 18 of the 30 samples at levels ranging from 24% to 46% by weight. Only DEHP was detected in the hard type toys. It was found in 14 of the 30 samples at levels ranging

from 0.01% to 0.15% by weight. The levels of phthalate in 60% of squeeze type toys and 10% of hard type toys exceeded the allowed limit.

1. Introduction

Phthalates which are derived from 1,2-benzene dicarboxylic acid esters, are chemically neutral, highly fat solubility and have a low volatility. They are used mainly as plasticizers, where they are present in the polymer network between its porous cavities. Thus, phthalates are easily leached in to the environment during or after the product life time. Although the toxic effects of phthalates on humans are still not well known, chronic effects such as decrease in food consumption and body weight, increase in mortality, a dose related increase in organ weight of liver and kidney have been observed in animal studies. The United States of America, European Union and Japan have restricted the use of certain phthalates in toys used by children below 12 years of age to a limit of 0.1%.

In this study the level of six phthalates [dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), diisononyl phathalate (DINP) and diisodecyl phthalate (DIDP)] were determined in soft and hard toys obtained from shops in the Colombo central market between December 2009 and June 2010.

2. Methodology

All the collected samples were categorized according to visual appearance as squeeze toys and hard toys. The phthalates were determined using the method specified in the ASTM [1]. The sample was cut into a size not greater than 3 mm × 3 mm × 3 mm and soxhlet extracted for 6 hours with a 1:1 (v/v) mixture of dichloromethane: methanol. The extract was concentrated using a rotary evaporator and purified using florisil. The analysis was carried out by GC-MS. The GC-MS chromatogram was obtained in scan mode and then processed in SIS (Selective Ion Storage) mode. The identification was carried out using retention times and mass spectral data of compounds (Compound, Retention time/ minutes and m/z: DBP, 10.93, 149; BBP, 12.76, 149; DEHP, 13.56, 149; DNOP, 14.96, 149; DINP, 15.75, 293; DIDP, 16.95, 307). The respective calibration curves were plotted (2 – 30 ppm for BBP, DBP, DEHP, DNOP and 8 – 120 ppm for DINP, DIDP) using standards purchased from Sigma Aldrich, USA. The phthalates were quantified using the respective peak areas.

The percentage recovery was determined by spiking the 'test' samples (samples not containing phthalate) with varying concentrations [DBP, BBP, DEHP, DNOP (2 ppm, 5 ppm, 10 ppm, 20 ppm and 30 ppm) and DINP, DIDP (8 ppm, 20 ppm, 40 ppm, 80 ppm and 120 ppm] of phthalate standards and carrying out the analysis as given above. The limit of detection was determined using the method given in Skoog [2] and Miller [3].

3. Results and Discussion

The calibration curves for all of the phthalate standards were linear ($r^2 \geq 0.99$) in the investigated concentration range of 2 – 30 ppm for BBP, DBP, DEHP, DNOP and 8 – 120 ppm for DINP, DIDP. The percentage recoveries were within the accepted range of 70% to 120% and the percentage RSD was less than ≤ 20% for concentrations of DBP, BBP, DEHP, DNOP (2 ppm, 5 ppm, 10 ppm, 20 ppm and 30 ppm) and DINP, DIDP (8 ppm, 20 ppm, 40 ppm, 80 ppm and 120 ppm). The LOD obtained was: BBP, DBP, 0.003%; DEHP, DNOP, 0.002%; DINP, DIDP, 0.004%. These values are significantly lower than the regulatory limits for consumer products [4].

Only two phthalates (DBP and DINP) were detected in the squeeze type toys. They were found in 18 of the 30 samples at levels ranging from 24% to 46% by weight. DEHP was the only phthalate found in the hard type toys. It was detected in 14 of the 30 samples at levels ranging from 0.01% to 0.15% by weight. The levels of phthalate in 60% of squeeze type toys and 10% of hard type toys exceeded the allowed limit of 0.1% by weight.

The phthalate levels in 60% of squeeze type toys and 10% of hard type toys exceed the allowed level specified by the Consumer Product Safety Commission, USA. Squeeze type toys contain significantly higher amounts of phthalate than hard type toys, and may be a health risk for children.

4. Recommendation

- Sri Lanka should implement regulations for the import of plastic products for children.
- Manufacturers of plastic products should replace phthalate plasticizers currently in use with less toxic plasticizers.

References

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Fast responding polyaniline based humidity sensor

H.M.P.C.K. Herath[1], M.K. Jayananda[2], J.K.D.S. Jayanetti[2], D.P. Dissanayake[1]

[1]Department of Chemistry, University of Colombo

[2]Department of Physics, University of Colombo

Abstract

A humidity sensor based on polyaniline thin films deposited on chlorinated glass surfaces by chemical and electrochemical polymerization is reported. Electrochemically deposited polyaniline on a layer of chemically deposited polyaniline induces a fast response to humidity. The sensor exhibits fast recovery and sensitivity to the full range of humidity and could be employed to measure rapid changes of humidity in ambient air.

1. Introduction

Semiconducting organic polymers have received attention of the researchers due to their versatility easy synthesis and low cost. They have found applications as molecular wires, light emitting materials, solar energy converters and sensors. Polyaniline is one such organic polymer that has been extensively studied. It has been reported that the direct current electrical conductivity of dry polyaniline is dependent on the gaseous environment to which polyaniline is exposed [1]. Applications of polyaniline in hydrogen gas and