ANALYSIS OF ADIPATE PLASTICIZERS IN FOOD PACKAGING MATERIALS AND FOODS

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Introduction

A plasticizer is a substance which is added to a material to improve its processability, flexibility and stretchability. Phthalates and adipates are the most frequently used as a plasticizers of poly(vinyl chloride)(PVC). They are commonly used in films, in tubings, in liners and seals for bottle caps or lids, in printing ink and in pulp products. Recently, adipates have replaced the phthalates in the application field of food packaging, mainly because some of them induced testis toxicity and antiandrogenic effects. [1] However, among adipate plasticizers, di-(2-ethylhexyl) adipate(DEHA) are listed as chemical substances that may have endocrine-disrupting effects.[2] This work was undertaken to investigate the residue in food packaging materials and to survey the migration amount of the adipates from food packaging into foods.

Materials and Methods

Samples : A total of 105 food packages was sampled in all parts of Korea 2004. Samples collected included cligning wraps(PVC), seals for bottle caps(PVC), films for wrapping sausage(PVDC), bottles(PET, PP), containers(PP, PE), tea bags(pulp) and filters (pulp).

Materials : Diethyl adipate(DEA), dipropyl adipate(DPrA), dibutyl adipate(DBA), diisobutyl adipate(DIBA), bis-(2-butoxyethyl) adipate(BBEA) and bis-[2-(2-butoxyethoxy)ethyl] adipate(BBEEA) were obtained from Sigma Aldrich Chemical Co., USA.. Di-(2-ethylhexyl) adipate(DEHA), diisononyl adipate(DINA) and diisodecyl adipate(DIDA) were obtained from Wako Chemical Co., Japan.

Sample Preparation: In the case of the packaging materials made from PVC, 1.0g of sliced samples was dissolved in a small quantity of tetrahydrofuran. And 200mL of methanol was added into the resultant solution with agitating to remove the precipitated polymer through filtration. The filtrate was evaporated and made up to 10mL of internal standard solution(0.1mg/mL acetanilide/acetone solution). For the others made from PE, PP, PET, PVDC, pulp which cannot be dissolved in tetrahydrofuran, 1.0g of each sliced samples was placed in an extraction thimble and transferred to a Soxhlet apparatus. Tetrachloromethane was added to the apparatus and the samples were extracted for 8hr. After completion of extraction, the extracts were evaporated and made up to 10mL of internal standard solution.

Food samples contacted with packaging materials contained adipates were cut in pieces (5×5 cm and 0.5 cm thickness) and homogenized with 70% acetone 100mL. The liquid layer extracted with dichloromethane and acetone:hexane(1:1) 30mL, respectively. The combined extracts were evaporated and their residues were redissolved in 10mL of internal standard solution.

Instrumental Analysis : A simultaneous analysis of 9 adipates in food packaging materials was carried out by dual-column GC-FID system. This system provided with two chromatograms separated by two different polarity columns(HP-5 (0.25mm i.d.× 30m, 0.25um thickness) and DB1701 (0.25mm i.d.× 30m, 0.25um thickness)) at a single injection and made it possible to cross-check the identification of peaks. The oven temperature was maintained at 70℃ for the first 3min, then ramped at 10℃/min to 240℃ where it was held for 10 min. Also, the migration amount of DEHA into food was analyzed by GC-MSD(SIM) equipped with HP-5MS capillary column(0.25mm i.d.× 30m, 0.25um thickness) and the oven temperature followed GC operating conditions. The selected ion was m/z=129 for quantification and m/z=147 for confirmation of DEHA. The proposed method for DEHA migration test was validated with >0.996 of linearity in the ranges of 4-1,000ug/L, 1ug/L of detection limit and 80.1-97.2 % of recoveries.

Results and Discussion

Residue in materials : In this study, the residual amount of adipates was determined for 105 food packaging materials. DEHA was detected in all the 3 samples of PVC wrap at levels from 17.7 to 19.9%. And among the 52 seals for bottle caps, DEHA was detected in 11 samples at levels from 0.03 to 0.36%. No target plasticizers were detected in any of the 11 PVDC films for wrapping sausage, the 11 pulp products, and the other 28 food packages consisted of PE, PP, PET.

Migration into foods : The migration amount of DEHA was investigated for the retail foods packaged with PVC wraps containing DEHA. Low migration levels in 0.02 – 0.97mg/dm^2 were observed in vegetables and sea foods circulated in cold storage. However, higher migration levels in 16.05 – 38.92mg/dm^2 were observed in fatty foods packaged at high temperature such as pizza, cooked soybean curd, boiled fish pastes, potatoes.

Generally, plasticizers are fat soluble so that the extent of migration would be expected to increase with the fat content. The migration tendency which is increased with the fat contents of foods and their storage temperature was observed and the migration amounts of DEHA was dramatically increased with storage temperature.[3,4] Based on the existing toxicity data, the EU Scientific Committee for

Food(SCF) has stated a tolerable daily intake(TDI) for DEHA of 0.3mg/kg of body weight(EEC Commission 1993). Using the conventional procedure of the EEC Commission for the calculation of specific migration limits(SML), this TDI will result in an SML for DEHA $3mg/dm^{2,}$ corresponding to a concentration in the food of 18mg/kg. In almost all instances, the DEHA concentration detected in the fatty foods contacted with PVC wrap at a high temperature was found to be considerably higher than this level. Also, this study shows the similar migration levels to other reports on DEHA migration into delivery foods in Korea depending on various exposure conditions.[5]

References

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