Stability of Plastics Monomers in Food-Simulating Liquids under European Union Migration Test Conditions

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The stability of 24 plastics monomers permitted for use in the European Union (EU) for food contact applications was studied in food-simulating liquids under various heating regimes. The monomers were heated in each of the food simulants (distilled water, 15% ethanol, 3% acetic acid, and olive oil) under conditions stipulated in EU regulations for testing for compliance with migration limits. Of the 24 monomers studied, 21 showed a loss in one or more of the simulants: for 14 substances the loss was 50% or greater, and 6 of the monomers were completely lost under at least one of the exposure conditions tested. These studies indicate that EU regulatory controls for monomers are, in a number of instances, meaningless, since it can be demonstrated that the starting monomer will not be present at the end of the testing regime or is substantially lost, thereby not reflecting the true level of migration.

Keywords: *Monomers, stability, migration, simulants*

In the European Union (EU; previously the European Community, EC) plastics monomers for use for food contact materials are controlled through a positive list in EC Directive 90/128 (EEC, 1990) and its subsequent amendment (EEC, 1992). These regulations allow unrestricted use of most listed monomers, but in the case of 44 specified monomers use is restricted to circumstances in which migration of the monomer from the plastic is below stipulated limits known as specific migration limits (SMLs). In the cases in which SMLs are imposed, it is required that migration into one or more of the four EC food simulants—distilled water, 15% ethanol, 3% aqueous acetic acid, and olive oil—be evaluated under temperature and time regimes appropriate to intended conditions of use (EEC, 1982, 1993). These regulations are designed as safety measures for consumer protection, and the migration limits are based on toxicological assessment of the various monomers. Despite the fact that most plastics monomers are by their very nature reactive species, the regulations assume stability under testing conditions and make no allowance for possible loss during migration testing or for the fact that if there are losses, then reaction products may be formed which have toxicities similar to or greater than that of the parent substance.

Although methods of analysis have been published for some of the monomers that have SMLs, these are not validated methods with the necessary performance characteristics that would make them suitable for enforcement purposes, nor have they in all cases been developed with a view to measurement in the EC food simulants. Headspace gas chromatographic methods with various detection systems have previously been reported for acrylonitrile (Pasquale *et al.*, 1978; Gilbert and Startin, 1982; Lickly *et al.*, 1991), 1,3-butadiene (Startin and Gilbert, 1984; Van Lierop, 1985), styrene (Gilbert and Startin, 1981), 4-methyl-1-pentene (Tice, 1988), and vinylidene chloride (Hollifield and McNeal, 1978; Gilbert *et al.*, 1980). Gas chromatographic procedures have been published for the determination of acrylamide as its brominated derivative (Castle, 1993) and for monoethylene and diethylene glycol as trimethylsilyl ether (TMS) derivatives (Castle *et al.*,

1988) or underivatized (Kashtock and Breder, 1980). HPLC methods have been published for 2,2-bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether (BADGE) (Paseiro Losada *et al.*, 1991), bisphenol A (Peltonen *et al.*, 1986), melamine (Ishiwata *et al.*, 1987), and terephthalic acid (Tice, 1988). A colorimetric procedure has been reported for formaldehyde (Sugita *et al.*, 1990). The European Committee on Normalisation (CEN) is currently producing standardized methods of analysis for monomers based initially on validation of existing published procedures (Ashby, 1994), and the EU is funding the development of methods of analysis for those monomers for which procedures are not currently available (Goenaga, 1994).

Very little work has been published on the stability of monomers, although from the structures of many it is obvious that hydrolysis or oxidation may well take place readily under testing conditions which involve heating in an aqueous environment. Paseiro Losada *et al.* (1993) have studied the hydrolysis of BADGE in aqueous food simulants at temperatures between 40 and 60 °C and have found half-lives from 2 to 70 h, with greatest stability in ethanol and least in acetic acid. Hydrolysis of the oxirane rings has been shown to occur with BADGE (Simal Gandara *et al.*, 1993), and it has been shown that while BADGE migration can be demonstrated to be below regulatory limits, when due account is taken of hydrolysis products, migration of the parent compound would exceed the tolerance. Rather more anecdotal evidence of monomer reactivity comes from observations, for example, for vinyl chloride that spiked foods and simulants employed in a collaborative trial gave lower recoveries than anticipated (Biltcliffe and Wood, 1982). There has not, however, been any systematic examination of all of the EU monomers with restrictions in EC Directives 90/128 and 92/39 (EEC, 1990, 1992) with a view to establishing their stability under proposed test conditions.

In this paper we have established quantitative procedures for determining 24 monomers in food simulants, with emphasis on being able to determine changes occurring as a result of reaction with the simulant during typical testing regimes. The intention has been to provide

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Table 1. Monomers Employed in Stability Studies—Abbreviations Used in This Paper and Reference Collection Identification Numbers (Gilbert et al., 1994)

substance	abbrev	ref collection
acrylamide		121
acrylonitrile	AN	108
2,2-bis(4-hydroxyphenyl)propane	bisphenol A	040
2,2-bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether	BADGE	122
1,3-butadiene		117
caprolactam		042
diethylene glycol	DEG	006
1,2-dihydroxybenzene	1,2-DHB	106
1,3-dihydroxybenzene	1,3-DHB	045
1,4-dihydroxybenzene	1,4-DHB	002
4-4'-dihydroxybenzophenone	DHBphenone	003
4,4'-dihydroxybiphenyl	DHbiphenyl	028
ethylene glycol	MEG	037
formaldehyde		115
maleic acid		048
methacrylonitrile		086
4-methyl-1-pentene		101
propylene oxide		116
styrene		133
terephthalic acid	TPA	075
tetrahydrofuran	THF	
2,4,6-triamino-1,3,5-triazine	melamine	001
1,1,1-trimethylolpropane		004
vinylidene chloride	VDC	114

an overview of the reactivity of monomers controlled by EU regulations. This overview should direct attention to the question of whether reactivity has been given proper consideration in regulations. The results reported here might pre-empt wasteful method development and method validation where stability data indicate that the survival of the migrating monomer is improbable.

MATERIALS AND METHODS

Materials. Samples of monomers of established purity and mostly of commercial origin were obtained from the MAFF reference collection of positive list substances (Bush et al., 1993; Gilbert et al., 1994) and are listed in Table 1.

Preparation of Samples. Samples of monomers were in most cases prepared at the statutory limits (SMLs) in each of the four EU food simulants. However, when preliminary studies indicated that detection at the SML was not readily attainable, spiked simulants were prepared at higher concentrations. The con-

centrations used for the stability experiments are given in Table 2. Preparation involved addition to the simulant of a solution of each monomer in a suitable solvent (typically 100 μL). The solvent was selected according to the solubility of the monomer, its compatibility with the simulant to be spiked, and the suitability of the solvent with regard to the final method of determination to be used for each monomer. Table 2 lists the solvents selected. The spiked simulants were then subjected to specific heating regimes and analyzed alongside untreated control samples that had been prepared at the same time but stored in the dark at −20 °C. The control samples corresponding to those monomers to be analyzed by headspace gas chromatography were prepared just prior to analysis from the same stock solution which had been stored in the dark at −20 °C. All experiments with food simulants were conducted in triplicate. Experiments with all four simulants were conducted for 10 days at 40 °C. Aqueous-based simulants were used also at 100 °C for 60 min. Olive oil was used also at 150 °C for 30 min and at 175 °C for 120 min. These conditions of time and temperature were selected from recommended conditions of test (EEC, 1993). No attempt was made to exclude light during exposure to the simulants. Internal standard (where employed, see Table 2) was added after the exposure period and prior to chromatographic analysis.

Gas Chromatographic Analysis. The following GC columns were employed for analysis: column A, 17 m × 0.25 mm i.d. × 0.2 μm CP-Sil 5CB (a dimethylsiloxane phase); column B, 50 m × 0.32 mm i.d. × 1.2 μm CP-Sil 8CB (95% dimethyl-, 5% phenylsiloxane); column C, 50 m × 0.32 mm i.d. × 1.2 μm CP-Sil 19CB (85% dimethyl-, 7% cyanopropyl-, 7% phenyl-, and 1% vinylsiloxane); column D, 50 m × 0.32 mm i.d. × 1.2 μm CP-Sil 5CB; column E, 25 m × 0.32 mm i.d. PoraPLOT Q (styrene/divinylbenzene).

Headspace Gas Chromatographic Analysis. AN, methacrylonitrile, 1,3-butadiene, 4-methyl-1-pentene, propylene oxide, styrene, THF, and VDC were analyzed by headspace GC using a Dani 3950 static headspace sampling unit (Dani SpA, Monza, Italy) coupled to a Carlo Erba 4160 GC. Analysis was carried out using an FID, with the exception of AN and methacrylonitrile which were determined with a nitrogen/phosphorus-specific detector and vinylidene chloride which utilized electron capture detection (ECD). All samples were equilibrated at 70 °C for 2 h prior to headspace sampling, with the exception of oil samples for styrene analysis which were heated for 2 h at 120 °C. Automated headspace analysis was carried out by pressurizing the vial with helium gas, venting to the sample loop, and then switching the sample onto the GC system. The transfer manifold was operated at 120 °C, vial pressurization time of 10 s, auxiliary pressure of 0.2 bar, venting time of 5 s, and injection time of 2

Table 2. Monomer Concentrations, Solvents, and Internal Standards Employed for Stability Experiments

monomer	concn (mg/kg)	solvent addition	internal standard
acrylamide	0.1	water	methacrylonitrile
AN	0.02	propylene carbonate	propionitrile
bisphenol A	6	methanol	
BADGE	0.5	methanol	
1,3-butadiene	1	dimethylacetamide	n-pentane
caprolactam	20	methanol	
DEG	30	ethanol	1,4-butanediol
1,2-DHB	12	methanol	
1,3-DHB	2.4	methanol	
1,4-DHB	6	methanol	
dihydroxybenzophenone	6	methanol	
dihydroxybiphenyl	0.6	methanol	
MEG	30	ethanol	
formaldehyde	20	water	
maleic acid	60	ethanol	
methacrylonitrile	0.1	propylene carbonate	propionitrile
4-methyl-1-pentene	5	dimethylacetamide	
propylene oxide	6.3	dimethylacetamide	
styrene	2.8	diethyl ether	ethylbenzene
TPA	8.5	methanol	phthalic acid
THF	6	diethyl ether	
melamine	30	water	
trimethylolpropane	60	methanol	
VDC	0.2	dimethylacetamide	1-chloropropane

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s. The analysis of the volatile monomers was carried out under the following GC conditions:

monomer	column	temperature conditions
AN	B	40 °C/3 min, then 10 °C/min to 70 °C
methacrylonitrile	B	40 °C/3 min, then 10 °C/min to 70 °C
1,3-butadiene	C	isothermal at 50 °C
4-methyl-1-pentene	D	isothermal at 45 °C
propylene oxide	E	isothermal at 130 °C
styrene	B	isothermal at 80 °C
THF	C	isothermal at 80 °C
VDC	D	isothermal at 70 °C

A direct comparison of peak area ratios (monomer to internal standard) of the freshly prepared monomer solution compared to that stored or heated in simulant was made to give a measure of monomer instability.

Direct Injection Gas Chromatography. Acrylamide, DEG, MEG, maleic acid, and 1,1,1-trimethylolpropane were determined by GC either by derivatization of the monomer directly in aqueous simulants or from oil after extraction into water (1:1) and similar treatment. Samples for acrylamide analysis were brominated as previously described (Castle, 1993), extracted into ethyl acetate, and injected. DEG and MEG were silylated (Castle *et al.*, 1988) using bis(trimethylsilyl)trifluoroacetamide (BSTFA). Maleic acid was ethylated by heating with boron trifluoride etherate in ethanol. and 1,1,1-trimethylolpropane was silylated by treatment with BSTFA. Determination of the monomers was carried out under the following GC conditions:

monomer	column	temperature conditions
acrylamide	A	isothermal at 170 °C
DEG	A	60 °C 4 min, 25 °C/min to 120 °C
MEG	A	60 °C 4 min, 25 °C/min to 120 °C
maleic acid	A	45 °C 1 min, 10 °C/min to 100 °C
1,1,1-trimethyol-propane	A	45 °C 6 min, 20 °C/min to 80 °C, then 5 °C/min to 280 °C

HPLC Analysis. Analysis by HPLC employed a Gilson 305 pump and a Gilson 116 UV detector (Gilson, Anachem, Luton, U.K.). Injections (20 µL) were made at a solvent flow rate of 1 mL/min. Mobile phase and detector conditions are listed below. Detection of BADGE was achieved using a Perkin-Elmer LS-5 luminescence detector (Perkin-Elmer, Beaconsfield, U.K.). Detector output was recorded using a Spectra-Physics SP 4400 Chromjet integrator (Spectra-Physics, Crawley, U.K.). The following 5-µm particle size HPLC columns were employed for analysis: column F, 250 × 4.6 mm ODS2 (7% carbon loading); column G, 250 × 4.6 mm ODS1 (11% carbon loading).

monomer	column	mobile phase	detection
1,2-DHB	F	20% MeOH	277 nm
1,3-DHB	F	20% MeOH	277 nm
1,4-DHB	F	15% MeOH, pH 3.6 (acetate)	277 nm
DHBphenone	F	50% MEOH	294 nm
bisphenol A	F	60% MeOH	275 nm
DHBiphenyl	F	50% MeOH	264 nm
BADGE	F	70% MeOH	ex 283 nm em 313 nm
melamine	G	20% ACN, pH 3.0 (phosphate)	235 nm
caprolactam	F	50% MeOH	230 nm
terephthalic acid	F	15% MeOH, pH 3.6 (acetate)	242 nm

A direct comparison of peak area ratios (monomer to internal standard) of the freshly prepared monomer solution compared to that stored or heated in the simulant was made to give a measure of monomer instability.

RESULTS AND DISCUSSION

Methods of Analysis. In general, the principles of published procedures have been used as a guide to the
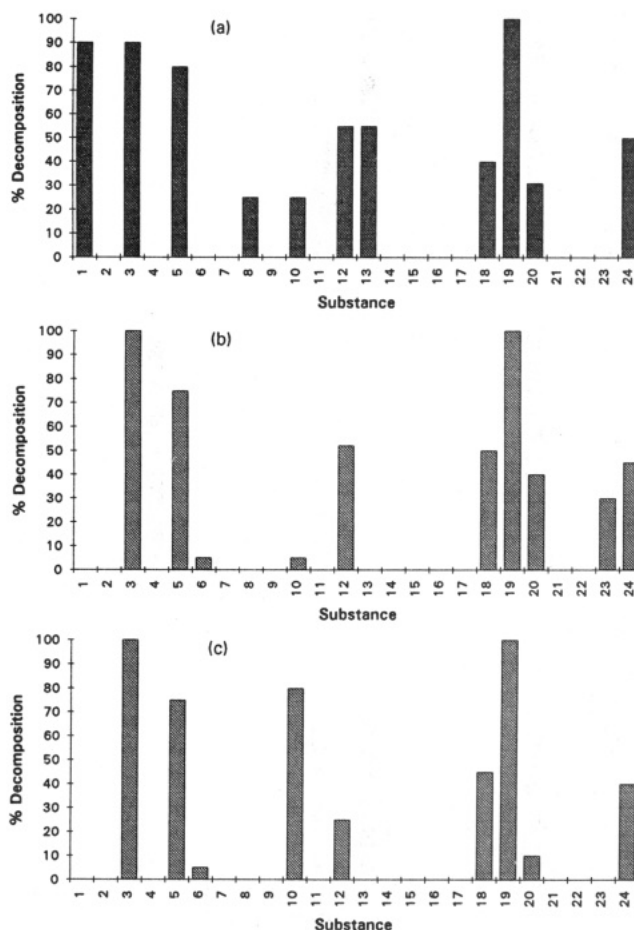

Figure 1. Stability of monomers shown as percent decomposition after storage in aqueous food simulants for (a) 10 days at 40 °C in distilled water; (b) 10 days at 40 °C in 3% acetic acid; and (c) 10 days at 40 °C in 15% ethanol. Monomer identification: (1) acrylamide; (2) AN; (3) BADGE; (4) bisphenol A; (5) 1,3-butadiene; (6) caprolactam; (7) DEG; (8) 1,2-DHB; (9) 1,3-DHB; (10) 1,4-DHB; (11) 4,4-DHBphenone; (12) 4,4-DHbiphenyl; (13) formaldehyde; (14) maleic acid; (15) MEG; (16) melamine; (17) methacrylonitrile; (18) 4-methyl-1-pentene; (19) propylene oxide; (20) styrene; (21) TPA; (22) THF; (23) 1,1,1-trimethylolpropane; (24) VDC.

best approach for analysis of the monomers in food simulants and published methods, where available, have not been followed exactly. To improve precision, internal standards have been employed wherever possible. Where methods were not previously available, but knowledge of volatility and polarity of the monomer has suggested a GC or HPLC approach, then the methodology for the most similar monomer has been applied. Eight monomers were analyzed by headspace GC, 5 by direct injection GC after suitable derivative formation, 1 by a colorimetric procedure, and the remaining 10 monomers by HPLC.

Where headspace GC was used for monomer analysis, preliminary work was carried out to establish that the aluminum crimp caps provided an effective seal and additionally that there was no evidence of adsorption losses of monomer by the headspace PTFE-faced rubber septa. This involved the preparation of standard solutions in headspace vials and storage with periodic reanalysis to ensure the analyte concentration did not decline.

Monomer Stability. The results for monomer stability are shown in Figure 1 for testing with aqueous simulants for 10 days at 40 °C, in Figure 2 for testing with aqueous simulants for 1 h at 100 °C, and in Figure 3 for testing with olive oil at 40, 150, and 175 °C. Of the 24 substances tested, only 3 showed no reaction under all of the test
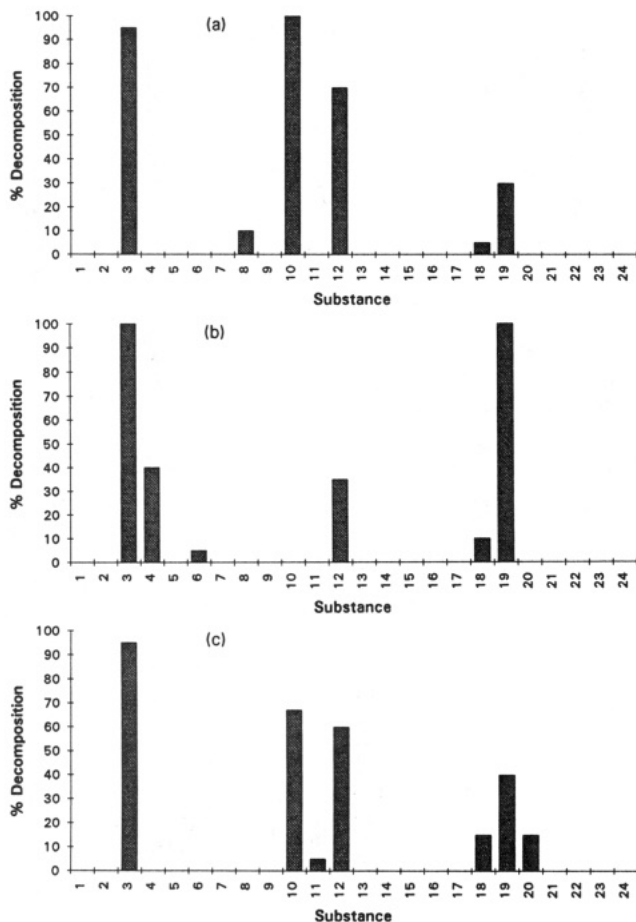
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Figure 2. Stability of monomers shown as percent decomposition after heating in aqueous simulants for (a) 1 h at 100 °C in distilled water, (b) 1 h at 100 °C in 3% acetic acid, and (c) 1 h at 100 °C in 15% ethanol. Monomer identification is by number as for Figure 1.

Figure 3. Stability of monomers shown as percent decomposition after storage or heating in olive oil fatty food simulant for (a) 10 days at 40 °C, (b) 30 min at 150 °C, and (c) 2 h at 175 °C. Monomer identification is by number as for Figure 1.

conditions. These substances were 1,3-dihydroxybenzene, tetrahydrofuran, and terephthalic acid. Similar chemical structures in general showed similar behavior in simulants with, for example, DEG and MEG showing losses only in olive oil at 175 °C, in both instances being of the order of 5–10%. Similarly, AN and methacrylonitrile only reacted in olive oil with losses of AN of 15% and 64% at 150 and 175 °C, respectively. Other compounds showing evidence of losses only with olive oil but apparently stable in aqueous simulants were maleic acid and melamine.

Of the six phenolic compounds investigated, 1,3-dihydroxybenzene did not show losses in any of the simulants, while 1,4-DHB was unstable in all four simulants, although losses were less under acidic conditions. 1,2-DHB reacted in water and olive oil at elevated temperatures, while DHBphenone showed a slight reaction (5% loss) only in aqueous ethanol. DHbiphenyl reacted in all of the aqueous simulants but not in olive oil. Coloration was evident as a result of apparent reaction undergone by some of the phenolic compounds, indicative of quinone formation. This is supported by the lack of reactivity of 1,3-DHB, which cannot be similarly oxidized, and the apparent greater stability of these phenols under acidic conditions. The possibility exists of these quinones undergoing further reaction to form dimers. It is possible that the decomposition seen for some of the phenolic substances contained a contribution brought about by light. The testing was conducted in subdued light, but light was not excluded totally. Migration test methods normally make no mention as to whether light should be excluded or not (Ashby, 1994). Testing materials in metal
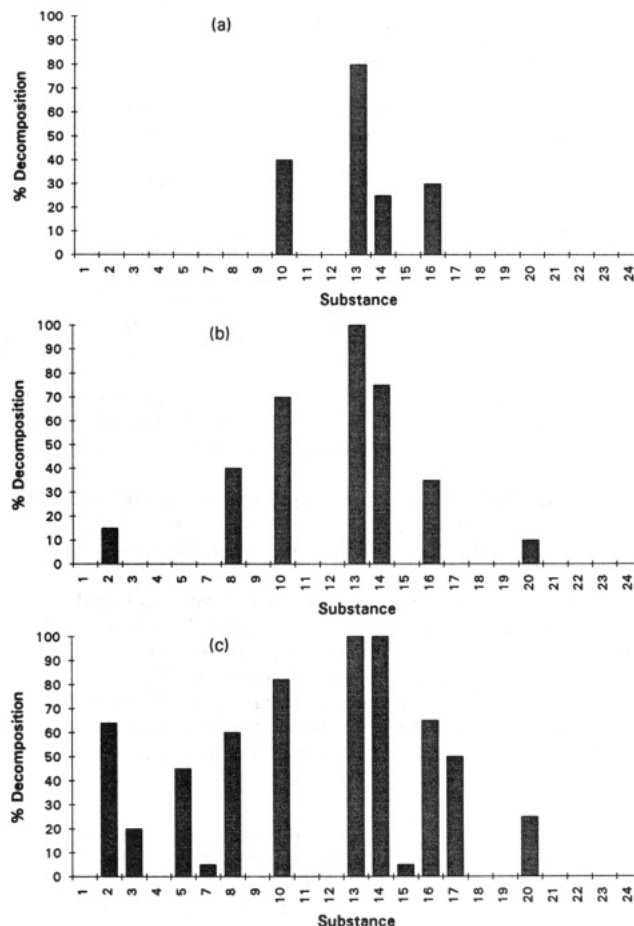
test cells clearly excludes light, but testing films as pouches or articles by filling can allow exposure of the simulant to light.

The results in this paper for the stability of BADGE, with losses of 90–100% in all aqueous simulants and 15–25% in olive oil at 175 °C, confirm previous observations (Paseiro Losada et al., 1993) and are consistent with the observation of greatest reactivity under acid conditions. The ease of hydrolysis of the epoxide group was further evidenced by the losses observed for propylene oxide, with 100% loss even in unheated acetic acid control solutions—presumably forming 1,2-propanediol. No losses of propylene oxide were evident when heated in olive oil, which is consistent with losses occurring by hydrolysis.

The work reported in this paper clearly demonstrates that, for 21 of the 24 monomers examined, testing under the stipulated EU test conditions will lead to monomer loss which was not forseen or taken into account when the regulations were drafted. It means that in some instances (e.g., for BADGE, which undergoes 100% loss) it would be impossible, irrespective of the extent of migration, to fail the statutory limit on monomer levels in the simulant. Two issues arise as a result of this work: first, whether it is worthwhile expending effort under the CEN program (Ashby, 1994) on developing validated methodology for monomers that are known to be inherently unstable in food simulants; and second whether more consideration should be given to determining the identity and toxicological significance of the reaction products which are ultimately the substances ingested by the consumer as the result of food contamination by migration.

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