P3TIR/P.95/2007

CHEMICAL CHARA CTERISTICS OF GAMMA IRRADIATED FOOD CONTACT RESIN POLYMERS

Z. Irawati, E.Miller, J.Hannecart, A.Chandrase and G. Sadler

AKTERISTIKA KIMIA DARI POLIMER RESIN BAHAN PENGEMAS
ANAN YANG DIIRADIASI GAMMA

Z. Irawati*, E.Miller**, J.Hannecart**, A.Chandrasekar** dan G.Sadler**

TRAK

KARAKTERISTIKA KIMIA DARI POLIMER RESIN BAHAN PENGEMAS ANAN YANG DIIRADIASI GAMMA. Metode karakteristika produk radiolisis y fat racun pada 3 jenis polimer resin yang diiradiasi gamma telah diteliti. Setiap je yaitu etilen vinil alcohol, Vista CON dan Nilon 12 dihaluskan, lalu dikondisikan n oven vakum pada suhu 40°C semalam, dan diiradiasi dengan dosis 25 kGy p kamar. Sampel kemudian diekstraksi dengan alat GC/MS yang dihubungkan den *matic Thermal Desorption (ATD).* Hasil yang diperoleh kemudian di karakterisasi ntifikasi sesuai dengan referensi pustaka *data base*. Komponen yang ditemu gian besar adalah terdiri dari unsur hidrokarbon dan turunannya. Larutan standar y akan unttuk mengidentifikasi resin yang diiradiasi diformulasikan dan diganda i dengan *FDA threshold of regulation.* Alkohol, asam, aldehid, keton dan alkena masi ng dilarutkan ke dalam 1,2,4-trichlorobenzene kemudian dielusikan bersama-sa el dan 2 larutan standar yang disertakan. Hasil yang diperoleh menunjukkan ba gian besar jenis komponen radiolitik dari sampel yang diteliti terdiri dari alko id, keton dan asam karboksilat. Pembentukan komponen tersebut akan bertam ngkatnya waktu ekstraksi. Terlihat pula bahwa kondisi peralatan ,metode GC/MS serta ATD *sequence* yang berbeda akan sangat berpengaruh pada data hasil ana . Response Factor yang diperoleh berdasarkan konsentrasi atom C yang ditarget meningkat dengan bertambahnya jumlah atom C, akan tetapi kemudian menu dah atom C kesepuluh.

kunci : makanan iradiasi, pengemasan, polimer resin

HEMICAL CHARACTERISTICS OF GAMMA IRRADIATED FOOD CONTAC RESIN POLYMERS

Z. Irawati*, E.Miller**, J.Hannecart**, A.Chandrasekar** and G.Sadler**

TRACT

CHEMICAL CHARACTERISTICS OF GAMMA IRRADIATED FO TACT RESIN POLYMERS. Characterization methods of potential toxic radiol cts of gamma irradiated three different resin polymers have been carried out. Ethyl alcohol (EVOH), Vista CON, and Nylon 12 resins were ground into fine powder fo ctively, then conditioned in a vacuum oven at 40°C overnight and followed by gam ation at a dose of 25 kGy room temperature prior to its analysis. The samples w cterized and were extracted on a GC/MS instrument coupled with Automatic Therm ption (ATD). The individual organic compounds within the polymers both before a irradiation were identified by using a computerized reference library data base. T unds observed in irradiated resins were mostly hydrocarbon derivatives. Standa n used for these classes was formulated in order to represent multiple of FDA thresho ulation. Various chemical compounds from the predicted radiolytic products i. ls, acids, aldehydes, ketones, and alkenes were respectively dissolved in 1,2,

results show that the identified compounds found in irradiated resin polymers v
ocarbons, alcohols, aldehydes ,ketones, and carboxylic acids. It is also obvious from
cular results that any document applied for analysis as well as GC/MS method, A
ods, and ATD sequence would give various differences in the retention time, molecular we
eak area of each finding compounds. Response Factor based upon concentration of C-atom
t analyte shows an increase by increasing the number of C-atom but it shows a decrease after

KARAKTERISTIKA KIMIA DARI POLIMER RESIN BAHAN PENGEMAS MAKANAN YANG DIIRADIASI GAMMA

Z. Irawati*, E.Miller, J.Hannecart**, A.Chandrasekar** dan G.Sadler****

RAK

KARAKTERISTIKA KIMIA DARI POLIMER RESIN BAHAN PENGEMAS
ANAN YANG DIIRADIASI GAMMA. Metode karakteristika produk radiolisis ya
at racun pada 3 jenis polimer resin yang diiradiasi gamma telah diteliti. Setiap je
yaitu etilen vinil alcohol, Vista CON dan Nilon 12 dihaluskan, lalu dikondisikan
oven vakum pada suhu 40°C semalam, dan diiradiasi dengan dosis 25 kGy pa
kamar. Sampel kemudian diekstraksi dengan alat GC/MS yang dihubungkan deng
atic Thermal Desorption (ATD). Hasil yang diperoleh kemudian di karakterisasi d
tifikasi sesuai dengan referensi pustaka *data base*. Komponen yang ditemuk
an besar adalah terdiri dari unsur hidrokarbon dan turunannya. Larutan standar ya
kan unttuk mengidentifikasi resin yang diiradiasi diformulasikan dan digandak
dengan *FDA threshold of regulation*. Alkohol, asam, aldehid, keton dan alkena masi
g dilarutkan ke dalam 1,2,4-trichlorobenzene kemudian dielusikan bersama-sa

atnya waktu ekstraksi. Terlihat pula bahwa kondisi peralatan ,metode GC/MS dan rta ATD *sequence* yang berbeda akan sangat berpengaruh pada data hasil analisa esponse Factor yang diperoleh berdasarkan konsentrasi atom C yang ditargetkan eningkat dengan bertambahnya jumlah atom C, akan tetapi kemudian menurun atom C kesepuluh.

ODUCTION

Irradiation is an effective technology for reduction and elimination of foodbor
ens may cause foodborne diseases. Food irradiation recently received an increase
t after FDA approved red meat irradiation in 1997 (FDA,1997). To preve
amination the food should be pre packaged then irradiated prior to shipping a
ution. Selection of packaging materials for use in food irradiation depends on t
nce or stability of the material to chemical changes when it is irradiated
ercial doses. The chemical compounds initially present and/or the degradation produc
l upon irradiation could migrate into food during storage and pose a safety risk.

As a result, a pre market safety evaluation by the FDA for the material is require
via food additive petition or exemption under the Threshold Regulation Polic
dless of evaluation procedures, chemical composition and migration data are require
se the number of FDA-approved food packaging materials for irradiation is limited
nd most were approved in the 1960's the suitability and safety for newer packagi
als for irradiation has not been established. This has become an impediment to larg
mplementation of food irradiation. Although gamma irradiation is currently the mo
on process, the packaging material to be used for irradiated foods should be proper

ERIALS AND METHODS

rials

Three different types of resin polymers, i.e., ethylene vinyl alcohol (ETOH), Vi
, and Nylon 12 as selected food packaging materials were ground respectively i
er, of 0.5 mm diameter, then used as starting samples prior to radiation sterilizati
e samples were obtained from food packaging industry in the USA.Qualification d
GC/MS methods and *nbs75k.l* as data base library were applied in order to ident
resence of certain chemical compounds in the irradiated samples. Various orga
ounds [1-4] such as alcohols (methanol, 1-propanol, 2-propanol, 1-butanol, 1-pentar
tanol, 3-heptanol, 1-nonanol, 2-nonanol, 1-undecanol, 2-undecanol, 6-undecanol,
anol, and 1-pentadecanol), acids (acetic, propanoic, butanoic, pentanoic, heptano
oic, undecanoic, and pentadecanoic), aldehydes (pentanal, octanal, decanal,
anal), ketones (2-butanone, methyl isobutyl ketone, 2-heptanone, 2-nonanone, and
anone), alkanes (pentane, hexane, cyclohexane, n-heptane, n-nonane, n-undeca
ane,, tetradecane, hexadecane, and tetracosane). Standard solutions used were
osane (10 ng/10µl),

R Benzophenone (50µl/5 ml), and 1 TOR Dibutylphtalate (8.62µl/5 ml). Benzophen

ation treatment

The γ -irradiation was conducted at Sterigenics International, as a commer
iator in Schamburg, Illinois using ^{60}Co as a source and the dose rate was 3 kGy/h. D
rmity was 1.03. Far west dosemeter was applied during the radiation process.

ation of radiolytic products and relative response factor

Both irradiated and unirradiated samples were respectively extracted for 1 and 20 n
C/MS thermal extraction system in order to get good separation and peak resolution
btained chromatogram, and to assure the best representation for polar and non pc
ounds. Tetracosane was applied as internal standard at level of 10 ng/10μl. Regarding
above results, the work was then continued to develop quantification method ba
relative response factor. Relative response Factors can be calculated according to
wing equation :

$$RRF = \frac{AcCis}{AisCc} \qquad [5]$$

The obtaining RRF value of each organic compound is considered acceptable in
e < 0.76. The various organic compounds were separately prepared at different multi
e FDA's USA Threshold of Regulation (TOR) values i.e., 0.25; 0.50; 1.00; 5.00; 10.
25.00 respectively. Calculation of individual internal standards were prepared
alent to 1 TOR in each syringe injection. Benzophenone at 25 TOR was prepared
25 ml (≅ 1.1148g) of the standard solution, and benzophenone at 1 TOR was prepa
ding to the following method : 4.46 g benzophenone was diluted in 25 ml orga
t. The quantity (g) for 1 TOR in 5 ml solution was : $1.1148/(25x5) = 8.92x10^{-3}$ g. Fi
e of 1 TOR benzophenone was : $(0.00892x25)/4.46x\mu l = 50\mu l$. Dibutylphtalate has p
at 99% degree of purity. Volume at 1TOR of this standard in 5 ml solvent w
ted as : $(8.92x10^{-3})/(1.045x0.99)\mu l = 8.62\mu l$.

The instrument condition used for qualification sample resin polymers was set up
: temperature injection, detector and oven temperatures were at 260, 280, and 325°
ively. Purge time was 1 min; holding time 6 min. at 12°C then elevated to 250°C
time for 49 min. The carrier gas used was Helium at flow speed 1 ml/min. Type o
olumn was a 60 m ZB wax with internal diameter of 0.25mm. Maximum elution tim
sample was 70 min. The dynamic thermal extraction in the samples was carried ou
different times, i.e., 1 and 20 min. respectively. A GC/MS

rties, presence of additive, and temperature applied during measurement. Unsaturat
xylic acid production shows an increase by increasing time induced by therm
dation. The result in the irradiated sample also shows the increasing some alipha
carbons as well as saturated and unsaturated hydrocarbons. However, the presence
idant or other filler compounds added in the resin during the process in the factory su
ylated hydroxy toluene (BHT), $C_{15},H_{24}O$, play an important role in order to reduce t
ion process during irradiation [1-3]. The action of antioxidants might be to combi
with radiation generated free radicals in the irradiated resin polymer or to transfor
radicals into inactive species. BHT might inhibit the formation of carboxylic acids
ted polymers. BHT is insoluble in water, freely soluble in some alcohol groups, a
ther hydrocarbon solvents. BHT is more soluble in food oil and fats [6].

The result shows in Table 3 indicating the presence of caprolactam ($C_6H_{11}NO$)
ted Nylon 12 caprolactam is a non-reacted monomer and having low molecular weig
uble in water and chlorinated hydrocarbons, cyclohexene, and petroleum fractions. It
r synthetic fibres of the polyamide type in the plastic manufacture. It is obvious fro
ticular results that any document applied during the analysis using GC/MS metho
injection temperature, ramp, and type of column, ATD method and ATD sequenc
give significant differences in the elution pattern, retention time, and

c. Alcohols : methanol (±5.88), isopropyl alcohol (± 6.76), 1-propanol (±9.67), butanol (±12.04), 1-pentanol (±14.06), 3-heptanol (±14.73), 1-heptanol (±17.01), 2-nonanol/undecanol (±17.83), and 1-pentadecanol (± 25.87).

d. Acids : acetic (±17.01), propanoic (±18.12), butyric (±19.19), valeric (±20.43 heptanoic (±22.60), nonanoic (±24.78), undecanoic (±25.52), and pentadecano (±27.47).

e. Aldehydes : pentanal (±8.18), octanal (±14.72), decanal (±17.66), and undecan (±18.93).

f. Ketones : 2-butanone(±5.90), methyl isobutyl ketone (±8.75), 2-heptanor (±8.75), 5-nonanone (±15.24), and 2-nonanone/2-undecanone (±16.17).

g. Alkanes : pentane (±2.20), hexane (±4.36), cyclohexane (±6.83), n-heptar (±8.51), n-nonane (±13.45), n-undecane (±16.89), tridecane (±19.62), tetradecar (±20.84), hexadecane(±23.10), and tetracosane (±25.11).

The relative response factor was calculated using the formulation resulted that th show an increase by increasing the number of atom carbon, but the RTF show se after Carbon number 8-10. This result suggested that the injector temperature has

ble 1.Identification of organic compounds in irradiated EVOH by thermal extraction at 1 and 20 minutes respectively analysed by GC/MS

Resin Polymers/extr. min).	Type of identified compounds*	
	Control	Irradiated at 25 kGy
EVOH/(1 min).		
	CO_2	CO_2
	- α methyl styrene	- α methyl styrene (-50%)
	cyclohexanol 3,5 dimethyl	-
	acetic acid	acetic acid
	butanoic acid butyl ester	-
	Propanoic acid 2 methyl-2 ethyl 2-hyd.	Propanoic acid 2 methyl butyl ester
	Propanoic acid 2 methyl	Propanoic acid 2 methyl
	2,2-dimethyl	2,2-dimethyl
	Butylated hydroxy toluene	Butylatedhydroxy toluene
	phenol	Phenol
	-	Decanoic acid
	2,4diphenyl-4methyl1 (E) pentene	2,4diphenyl-4methyl1 (E) pentene
	eicosane	-
	docosane	Docosane
	Dibutyl-phtalate	Dibutyl-phtalate
	tetracosane	Tetracosane
	Henelcosane (-50%)	Henelcosane
	-	Heptacosane
	-	Benzoic acid
EVOH/(20min).	CO_2	CO_2
	Isopropyl alcohol	-
	ethanol	Ethanol
	2-butanol	2-butanol
	Benzene-1-methylethyl (25%)	Benzene-1-methylethyl
	3-hexanol	3-hexanol
	Benzene-tert-butyl-ol	Benzene-tert-butyl
	-	Benzene-2-methylpropyl

Table 1. Identification of organic compounds in irradiated EVOH by thermal extraction at 1 and 20 minutes respectively analysed by GC/MS (*cont.'d*)

Resin Polymers/extr. (min).	Type of identified compounds*	
	Control	Irradiated at 25 kGy
EVOH/(20 min).	**Hexanoic acid**	**Hexanoic acid**
	Heptanoic acid	**Heptanoic acid**
	Nonanoic acid	**Nonanoic acid**
	2,4-diphenyl4-methyl-2(z) pentene	**2,4-diphenyl4-methyl-2(z) pentene**
	tetracosane	**Tetracosane (+10%)**
	2,4-diphenyl4-methyl-1(E) pentene	**2,4-diphenyl4-methyl-1(E) pentene**
	2,4-diphenyl4-methyl-2(E) pentene	**2,4-diphenyl4-methyl-2(E) pentene**
	Docosane	**Docosane**
	henelcosane	**Henelcosane**

*)1. bold letters express similar compounds are presence both in control and irradiated samples
2. percentage number between the bracket expresses increasing (+) or decreasing(-) of peak area.

Table 2.Identification of organic compounds in irradiated Vista CON by thermal extraction at 1 and 20 minutes respectively analysed by GC/MS

Resin Polymers/extr. (min).	Type of identified compounds*	
	Control	Irradiated at 25 kGy
Vista CON (1min).	CO_2	CO_2
	-	Dodecane
	-	1-undecene 2-methyl
	-	Tridecane
	Cyclopentane 3-hexyl 1,1-di-methyl	Cyclopentane 3-hexyl 1,1-di-methyl
	-	Tetradecane
	Cyclohexane 1,5-diethenyl	Cyclohexane 1,5-diethenyl

Table 2.Identification of organic compounds in irradiated Vista CON by thermal extraction at 1 and 20 minutes respectively analysed by GC/MS (*cont.'d*)

Resin Polymers/extr. (min).	Type of identified compounds*	
	Control	Irradiated at 25 kGy
Vista CON (20 min).	CO_2	CO_2 (+150%)
	Dodecane	Dodecane
	Tridecane	Tridecane
	-	1-undecene-2-methyl
	cyclopentane	-
	Tetradecane	Tetradecane
	-	1-dodecanol 2 methyl
	Pentadecane	Pentadecane
	-	2 methyl, 1 tetradecane
	hexadecane	Hexadecane
	-	Hexadecane 2 methyl
	heptadecane	Heptadecane
	octadecane	Octadecane
	nonadecane	Nonadecane
	Butylatedhydroxy toluene	-
	-	Tetradecanal
	-	Docosane
	-	2-heptadecanone
	-	Decanoic acid
	-	Tetracosane
	-	Dodecanoic acid
	phenol	phenol
	-	1-octadecene
	cyclohexadecane	-
	Tetradecanoic acid	Tetradecanoic acid (+150%)
	-	Pentadecanoic acid
	Hexadecanoic acid	Hexadecanoic acid (+200%)
	Octadecanoic acid	Octadecanoic acid (+50%)

*)1. bold letters express similar compounds are presence both in control and irradiated samples
2. percentage number between the bracket expresses increasing (+) or decreasing (-) of

Table 3.Identification of organic compounds in irradiated Nylon 12 by thermal extraction at 1 and 20 minutes respectively analysed by GC/MS

Resin Polymers/extr. (min).	Type of identified compounds[*]	
	Control	Irradiated at 25 kGy
Nylon 12 (1min).	CO_2	CO_2 (+ 50%)
	-	Acetaldehyde
	-	2-butanone
	-	Pentanal
	-	1-butanol
	-	α-methyl styrene
	Acetic acid	**Acetic acid (+50%)**
	-	Formic acid
	-	Propanoic acid
	-	Butanoic acid
	acetamide	**Acetamide (+50%)**
	-	Octanoic acid
	hexadecane	-
	-	Nonanoic acid
	docosane	**Docosane**
	heptadecane	-
	tetracosane	**tetracosane**
	-	Benzoic acid
	-	Docosane
	-	Hexacosane
	-	heneicosane
Nylon 12 (20 min).	CO_2	CO_2
	-	Pentanal
	-	Isopropyl alcohol
	-	1-butanol
	-	Pyridine (%)
	-	Tetradecane
	Acetic acid	**Acetic acid**
	-	Pentadecane

Table 3.Identification of organic compounds in irradiated Nylon 12 by thermal extraction at 1 and 20 minutes respectively analysed by GC/MS (*cont.'d*)

Resin Polymers/extr. (min).	Type of identified compounds*	
	Control	Irradiated at 25 kGy
Nylon 12 (20 min).	**Nonanoic acid**	**Nonanoic acid**
	-	caprolactam
	heptadecane	-
	tetracosane	**tetracosane**
	-	Benzoic acid
	-	Heneicosane
	heptadecane	-
	tetracosane	**tetracosane**
	-	Benzoic acid
	-	Heeneicosane
	heptadecane	-
	docosane	**docosane**
	heneicosane	-
	-	Heptacosane
	-	Dibutylphtalate
	-	benzamide
	Hexadecanoic acid	**Hexadecanoic acid**

*)1. bold letters express similar compounds are presence both in control and irradiated samples
2. percentage number between the bracket expresses increasing (+) or decreasing(-) of peak area.

LUSION

It can be concluded from the obtaining results that some radiolytic products have developed i
diated plastics. The *nbs 75k.l* data bank has the ability in order to identify some individu
compounds such as caprolactam found in irradiated nylon. some acids. ketones. alkanes . a
. Further work on the quantification of some radiolytic products in the irradiated plastics base
ponse factor needs to be done.

RENCES

CHALLA, R., SCHUTTLER,C. and BOGL, K.W., Effect of ionising radiation
polymers, A compilation of literature data. Part I. Food packaging materials. Instit
fur Sozialmedizin und Epidemiologie des Bundesgesundheitsamtes, Berlin (1992).

CHALLA, R., BOESS,C. and BOGL,K.W., Radiolysis products in gamma-irradiated
plastics by thermal desorption–GC-MS.Part I, Bundesinstitut fur gesundheitlichten
Verbraucherschutz und Veterinarmedizin, Berlin (1997).

CHALLA, R., BOESS,C. and BOGL,K.W., Radiolysis products in gamma-irradiat
plastics by thermal desorption–GC-MS.Part II, Bundesinstitut fur gesundheitlicht
Verbraucherschutz und Veterinarmedizin. Berlin (1997).

RREL, T.N., "Interpreting Spectra of Organic Molecules", A series of books in orga
chemistry, editor :R.G. Bergman, University Science Books, Mill Valley, Californ
(1988).