

Synergistic Stabilization of Food-Packaging Materials

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Abstract—Food is widely packaged with plastic materials to prevent microbial contamination and spoilage. Ionizing radiation is widely used to sterilize the food-packaging materials. Sterilization by γ -radiation causes degradation such as embrittlement, stiffening, softening, discoloration, odour generation, and decrease in molecular weight. Many antioxidants can prevent γ -degradation but most of them are toxic. The migration of antioxidants to its environment gives rise to major concerns in case of food packaging plastics. In this attempt, we have aimed to utilize synergistic mixtures of stabilizers which are approved for food-contact applications. Ethylene-propylene-diene terpolymer has been melt-mixed with hindered amine stabilizers (HAS), phenolic antioxidants and organophosphates (hydroperoxide decomposer). Results were discussed by comparing the stabilizing efficiency of mixtures with and without phenol system. Among phenol containing systems where we mostly observed discoloration due to the oxidation of hindered phenol, the combination of secondary HAS, tertiary HAS, organo-phosphite and hindered phenol exhibited improved stabilization efficiency than single or binary additive systems. The mixture of secondary HAS and tertiary HAS, has shown antagonistic effect of stabilization. However, the combination of organo-phosphite with secondary HAS, tertiary HAS and phenol antioxidants have been found to give synergistic even at higher doses of Gamma-irradiation. The effects have been explained through the interaction between the stabilizers. After γ -irradiation, the consumption of oligomeric stabilizer significantly depends on the components of stabilization mixture. The effect of the organo-phosphite antioxidant on the overall stability has been discussed.

Keywords—Ethylene-propylene-diene terpolymer, Synergistic mixtures, Gamma-sterilization and stabilization.

I. INTRODUCTION

THE unique properties of polyolefins, such as mechanical properties, transparency, low cost, durability, resistance to weathering and photo-degradation as well as biological attack and hydrophobicity, have contributed to their skyrocketing utility in different applications. In food packaging and biomedical field, they have been the choice of materials. These materials are mostly sterilized by γ -radiation which is used when materials are sensitive to the high temperature of autoclaving but compatible with ionizing radiation. The most commonly validated dose used to sterilize medical devices is 25 KGy [1]. However, sterilization of biomedical polymers by γ -radiation is also known to result in physical changes, including embrittlement, stiffening, softening, discoloration,

during the subsequent post-irradiation storage (on months to year's time scale) [6]. Fig. 1 shows the general pathways of degradation and stabilization where radical formation is initiating and vital step for polymer degradation.

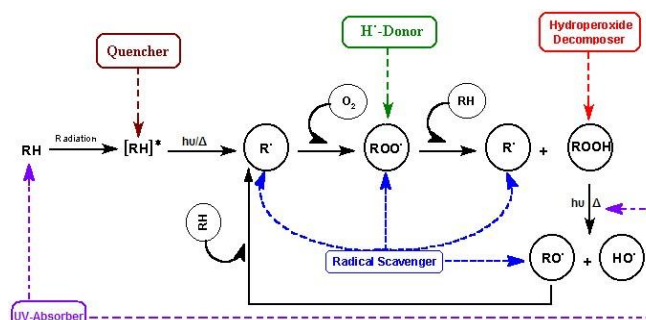


Fig. 1 General pathways of degradation and stabilization of polymers

Stabilization can be done at different stages by adding very small number of additives called as ‘stabilizers’. They are differing in their mode of protection or in the mechanism they inhibit the degradation and are classified as radical scavengers, antioxidants and hydroperoxide decomposers.

Hindered amine stabilizers (HAS) are widely used radical scavengers. The efficiency of HAS was first postulated to the ability of piperidine rings to oxidise into nitroxyl radical ($>NO\cdot$) which scavenges the polymer radicals responsible for degradation of polymers. They have multifunctional capabilities to scavenge radicals, forming complexes, quench excited state groups, localize in oxidized regions, associate with hydroperoxides and catalyze their decomposition. A substituted piperidine, was found to give good protection (little yellowing or embrittlement) against γ -irradiation as well as post-irradiation storage under accelerated test conditions (60 °C in air) [7]. Then, antioxidants are also widely used and most popular antioxidants in this area are hindered phenols (primary antioxidants) which are extremely effective at preserving physical properties of polymer during and after γ -sterilization but at the expense of yellow color formation [8]. The yellow color formation is attributed to the formation of quinonoids structures as seen in Fig. 2.

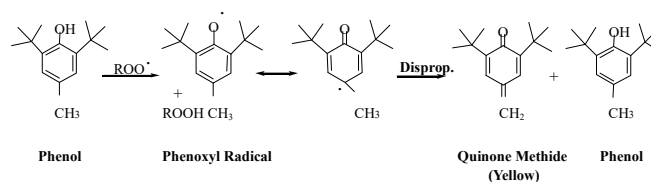


Fig. 2 Formation of quinonoids structures

older generation and decrease in molecular weight [2]-[5]. Embrittlement occurs not only during γ -irradiation, but also

The mechanism of phenolic antioxidants involves a chainbreaking donation of a hydrogen atom from the antioxidant to the reactive peroxy-radical. This produces a less-reactive resonance-stabilized phenolic radical. Each phenolic moiety is capable of trapping a total of two radicals before it is completely consumed. Unlike primary antioxidants, all secondary antioxidants work by decomposing reactive species like peroxides, they do not have the ability to trap radicals initially. Secondary antioxidants (organo-phosphites) act at the initiation stage of the radical chain mechanism to prevent the formation of radical products by decomposing the hydroperoxides to form stable nonradical species. However, there was an argument on the effectiveness and the role of organo-phosphite (hydroperoxides decomposer) was reported to be ineffective [9] and effective [10] in protecting polypropylene against γ -irradiation.

On the other hand, physical losses of antioxidants occur due to volatilization (especially at the high processing temperature), poor solubility, diffusion, and leachability when in contact with solvents during service [11], [12]. Migration of antioxidants to its environment (esp. direct contact with humans) gives rise to major concerns in case of food packaging plastics, packaging materials for pharmaceuticals and other medical application. This migration is associated health hazards and has received greater attention. Health authorities in Europe, USA and many other countries have strict regulations to control the use of additives in plastics used for food packaging [13], [14]. Thus, the use of stabilizers should be approved for food contact applications. Unlike stabilizers based on aromatic amines, phenolic antioxidants are approved for food contact applications [15]. It is well known that stabilization of polymer is accompanied by a loss of most of the effective stabilizers. This loss can be caused by either chemical consumption of the stabilizers during stabilization reactions and/or physical loss of stabilizer. Very short time protection was found with low-molecular weight HAS and long time protection with the oligomeric HAS [16]. Gugumus et. al. [17] determined the optimum molecular weight (MW) to be about 2700 for poly(1,2,2,6,6-pentamethyl-4-piperidyl acrylate) for light stabilization of polypropylene. Chmela et al. [18] had also been emphasizing the importance of the compatibility of the stabilizer with PP and concluded that the stabilizer mobility played an important role in the overall mechanism of stabilization of HAS in this substrate. It was reported that [19] approximately 95% molecules of oligomeric stabilizer were translationally immobile in the polymer matrix and it was explained that decreased efficiency of oligomeric stabilizers with increased molecular weight was as a result of reduced stabilizer mobility. Thus, there have been always some disadvantages in using single additive system such as compatibility, migration with low molecular weight stabilizers (esp. HAS), immobility with high molecular weight stabilizers, yellowing with phenolic antioxidants, reduced efficiency of organo-phosphites.

In recent years, the blending of the phenolic antioxidants with other stabilizers has become the interesting topic of research [15]. A blend of two additives is referred as 'synergistic mixtures' if the observed effect is greater than that of simple addition of the effects of the individual components. The opposite is also true

and defined as antagonism. Blends of stabilizers with same effective mechanism are referred to as homo-synergistic combinations. The most important are the hetero-synergistic combinations of stabilizers that have different effective mechanisms and complement with each other [15]. Considerable research has been dedicated to discovering system that could improve stabilization efficiency. Elsewhere, researchers were working on elucidating optimum blends or formulation of commercially available HALS with decomposers, UV and thermal stabilizers [20], [21].

In literature, the use of blends of stabilizers for γ stabilization was not yet attempted. Considering above said aspects, for the first time, we have aimed to stabilize the ethylene-propylene-diene terpolymer using synergistic mixtures of oligomeric stabilizers. For this purpose, we have used mixtures of primary antioxidants and secondary antioxidants, which are approved for food contact applications, and their selection has been based on different molecular weight. The ethylene-propylene-diene terpolymer is mixed with one oligomeric secondary-HAS, tertiary-HAS, hindered phenol and an organo-phosphite and γ -irradiated. The stabilizing efficiency of the synergistic mixtures was studied and has been discussed by comparing the system with and without phenolic stabilizers.

II. EXPERIMENTAL

A. Materials

Pellets of ethylene-propylene-diene terpolymer (40.6 molar % of ethylene content) were purified by refluxing with xylene under nitrogen atmosphere. The polymer was precipitated, with cold methanol and drying at 35°C in vacuum oven. These samples were assumed to be 'additive free'. Four different stabilizers supplied by M/s. Ciba-Geigy, Switzerland which are approved for food contact applications [22] are used in this study.

- i) Tinuvin-765, a low molecular weight tertiary HAS, bis(1,2,2,6,6-pentamethyl-4-piperidinyl sebacate), yellow liquid, (MW=508 g/mol), designated as (T):

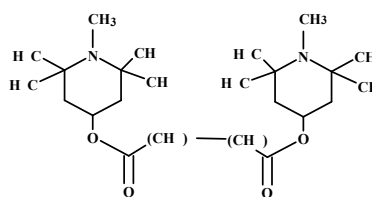


Fig. 3 Tinuvin-765 (T)

- ii) Chimassorb-944, an oligomeric HAS, Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl]-[(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl [(2,2,6,6-tetramethyl-4-piperidinyl)imino]], white powder, m p 115-125 °C, (2790 g/mol), Mn \approx 3000., designated as (C):

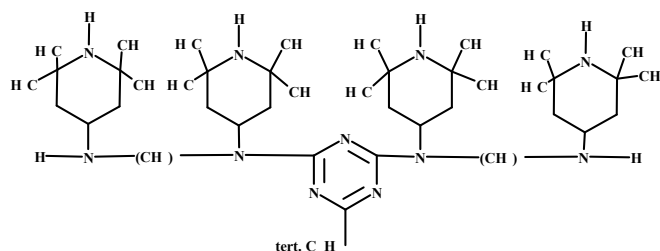


Fig. 4 Chimassorb-944 (C)

- iii) Irganox-1010, a hindered phenol, tetrakis[methylene 3-(3', 5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane, (MW= 1178) designated as (X):

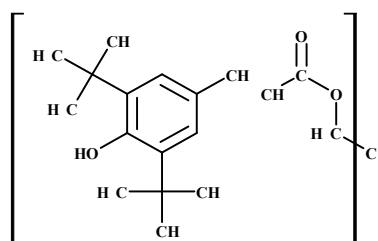


Fig. 5 Irganox-1010 (X)

- iv) Irgafos-168, an organo-phosphite, IV, tris(2,4-di-tertbutylphenyl) phosphite, (MW= 649.9) designated as (S):

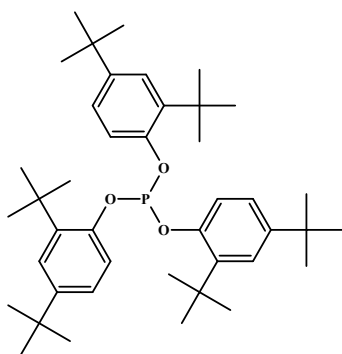


Fig. 6 Irgafos-168 (S)

B. Mixing of Stabilizers and Preparation of Specimens

The weighed amount of stabilizers was dissolved in chloroform and mixed with the required amount of dried ethylene-propylene-diene terpolymer for better distribution of stabilizers through the polymer powder, and chloroform was evaporated and dried in a vacuum oven at 50°C. After drying, this polymer was melted and mixed through micro compounder (DSM, The Netherlands) for 5 min. Keeping the ratio between polymer and stabilizer 99.6: 0.4, and ratio between the stabilizers as 1:1 in case of two components, 1:1:1 for case of three components and ratio 1:1:1:1 four component system, the samples were prepared and their formulation were tabulated in Tables I and II. The compounded samples were molded into sheets using a compression-molding machine at 150 kg/m² pressure at 130°C.

TABLE I
PHENOL FREE SYSTEM

S.No	Sample Polymer		Stabilizers %			
	Code	%	Irganox -1010	Chimassorb944	Tinuvin765	Irgafos168
1	C		-	0.4	- 0.4	-
2	T		-	-	-	- 0.4
	S	99.6	-	-		
	CT		-	0.2	0.2	-
	CS		-	0.2	-	0.2
	CTS		-	0.133	0.133	0.133

TABLE II
PHENOL SYSTEM

S.N	Sampl e Code	Polymer %	Stabilizers %			
			Irganox101 0	Chimasso r b-944	Tinuvin76 5	Irgafos16 8
7	X		0.4	-	-	---
8	CX	99.	0.2	0.2	-	
9	CTX	6	0.133	0.133	0.133	
	CXS		0.133	0.133	-	0.133
	CTXS		0.1	0.1	0.1	0.1

C. γ -Irradiation

The specimens were kept in a well type ⁶⁰Co gamma radiation chamber for uniform exposure. The samples were irradiated at different doses: 25 (sterilization dose), 50, 75 and 100 KGy (dose rate 1.6 KGy h⁻¹) at room temperature in air.

D. FT-IR Spectroscopy

FT-IR (Fourier transform infrared 16 PC spectrometer) was used to characterize the chemical changes caused by γ radiation in the polymer specimens. Oxidation products were identified and quantified and our interest was mainly focused on the changes in the carbonyl region (1600-1800 cm⁻¹) to follow γ -induced oxidation. The IR spectrometer was used to measure the concentration of carbonyl compounds in the polymer specimens at 1720 cm⁻¹. A value of 220 L mol⁻¹ cm⁻¹ was used for absorption coefficient [23]. The spectrometer was operated at a resolution of 4 cm⁻¹. The oxidized specimens were analyzed immediately to minimize the post γ -effect.

E. Mechanical Properties

The changes in the tensile properties were measured by a universal testing machine, Instron Model 4201. Elongation at break was determined from stress-strain curves. The cross speed used was 10 mm min⁻¹. The specimens used were 100 mm length, 10 mm width and the gauge space 50 mm. The results of each sample were taken as the average of five specimens.

F. Color Measurements

Yellowness index (YI) was determined in accordance with ASTM D1925 [24] by reflectance measurements using Color Mate HDS Colorimeter (Milton Roy, USA) with integrating sphere. The samples were placed in the reflectance part of a sphere using a standard white ceramic as reference tile. The instrument is designed to give direct yellowness index value on the basis of CIE standard illumination C (CIE 1931) 2° standard observer viewing [25]. It was obtained from the tristimulus values XCIE, YCIE and ZCIE relative to source C using the equation $YI = [100 (1.28 XCIE - 1.06 ZCIE)] / YCIE$. Several values of YI obtained from different parts of the samples were generally used to obtain an average value of the yellowness index.

III. RESULTS AND DISCUSSION

The stabilizing efficiency of incorporating more than one stabilizer into ethylene-propylene-diene terpolymer was characterized and discussed by comparing the results of stabilizer mixtures with and without phenolic antioxidants as well as individual systems.

A. Tensile Properties

Figs. 7 and 8 represent the changes in tensile properties of neat and stabilized samples before and after γ -sterilization with dose of 25 KGy. The stabilizing efficiency of phenol free system and phenolic system can be seen in Figs. 7 and 8 respectively, in terms of elongation at break (%). After 25 KGy γ -radiation, the decrease in the values of elongation at break (%) are observed for all the samples which can be attributed to the γ -induced oxidative degradation that would cause the chain scission of the polymer backbone [26]. After γ -sterilization, the elongation at break (%) of neat samples was observed to be lowest, while the samples with stabilizers have shown higher values of elongation at break (%). Among the samples which contain stabilizers, CTS samples have shown very less / marginal decrease in the value of elongation at break (%) which can be attributed to higher stabilization of that sample. In comparison, of the individual stabilizer system, the samples of 'S' have shown higher stabilization and the sample 'C' become liable to embrittlement. In case of binary additive systems, the samples of CS have shown higher value of elongation than that of CT in binary systems. It is also obvious that combination of sec-HAS and organo-phosphite [i.e. CS] exhibits synergistic improvement in stabilization than their individual stabilizers whereas CT shows antagonistic effect of stabilization. Addition of organo-phosphite 'S' to an antagonistic composition, [i.e. CTS] has shown significant increase in elongation at break (%). The effect of addition of hindered amines and organo-phosphite to hindered phenol containing samples can be seen in Fig. 8 where improved elongation at break (%) is observed. In phenol containing systems also, the presence of organo-phosphite 'S', shows the increase in elongation at break (%). Thus, it can be inferred from these (Figs. 7, 8), the increasing order of efficiency of the stabilization in terms of tensile properties i.e. protection against embrittlement can be $CT < CX < CTX < CXS < CTXS < CS < CTS$.

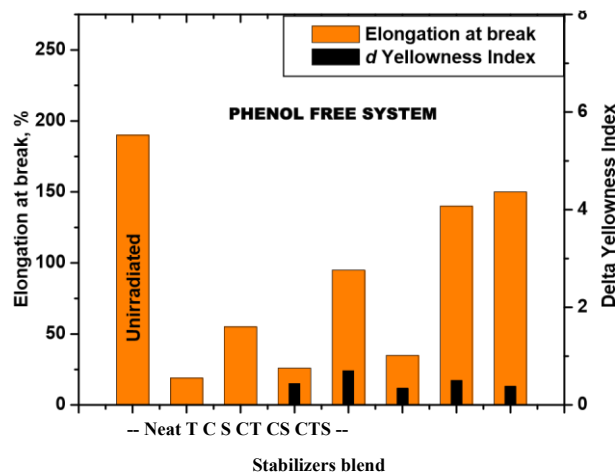


Fig. 7 Changes in tensile properties and yellow index of phenol-free system after γ -irradiation (25 KGy)

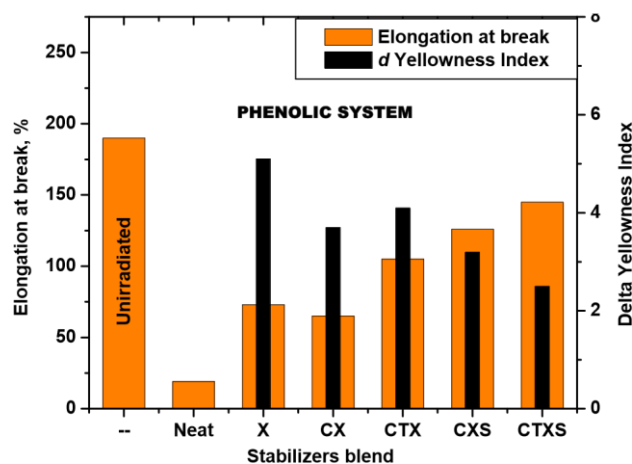


Fig. 8 Changes in tensile properties and yellow index of phenolic system after γ -irradiation (25 KGy)

B. Yellowness Index

The discoloration of neat and stabilized samples before and after γ -irradiation to a dose of 25 KGy is also represented in Figs. 7 and 8 in terms of delta yellowness index.

The yellowing phenomenon is observed predominantly with phenol containing systems, which can be attributed to the fact that hindered phenols are pronounced to undergo radioinduced oxidative degradation to give quinonoid structures which are assignable for discoloration of the samples. The effect addition of sec-HAS, tert-HAS and organo-phosphite (secondary antioxidant) to hindered phenol (primary antioxidant) can be seen in Fig. 8 where reduction in yellowing was observed. The significant reduction in yellowing by the addition of secondary HAS can be observed in system 'CX' which may be attributed to the radical scavenging effect of added stabilizer. By comparing the YI values of mixtures from Fig. 8, it can be inferred that the addition of organo-phosphite, to hindered phenol containing system reduced the yellowing. This can be attributed to the fact that organo-phosphite decomposes the hydro-peroxides to reduce further oxidation, and their reaction with oxidized products of

hindered phenol i.e. highly coloured quinonoids which are transformed into colorless benzenoid forms as shown in Fig. 9.

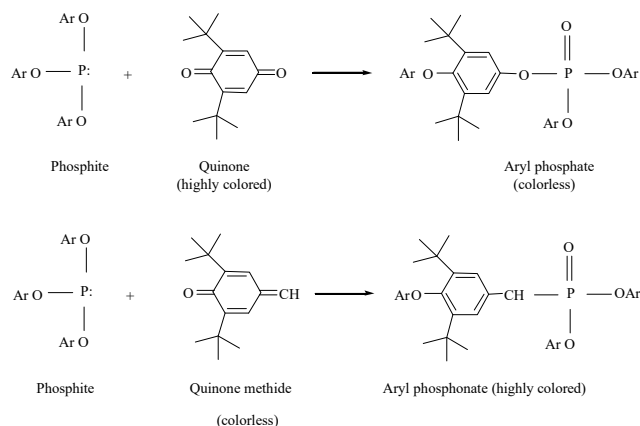


Fig. 9 Proposed mechanism for stabilization of benzenoid structure [27]

In addition, from the Fig. 8 the decreasing order of efficiency of the stabilization in terms of yellowing index, i.e. protection against discoloration can be represented as; CTXS > CXS > CX > CTX > X.

C. Carbonyl Group Evolution

The carbonyl group evolution upon γ -irradiation with different doses is plotted as shown in Figs. 10 and 11. It is observed from Fig. 10 illustrates the increase in concentration of carbonyl group (mmole L^{-1}) of neat sample and single stabilizer systems. It is clearly seen that the rate of increase in neat sample is higher than that of in single stabilizer systems

with increasing dose of γ -irradiation. Upto 25 KGy γ irradiation, for single-stabilizer systems, the increasing order in the rate of increase in carbonyl group is T > C > X > S i.e. the sample containing phosphite-based stabilizer (hydroperoxide-decomposer) 'S' is more stabilized against oxidation than others. Among hindered amine stabilizer (HAS), tertiary HAS (T) was more effective than secondary HAS (C). With increasing dose of γ -irradiation above 25 KGy, this stabilization efficiency order is affected and for 100 KGy γ -irradiated samples, this order is completely changed as S > C > T > X. This can be attributed the fact that there may be the consumption of stabilizers during γ -irradiation with higher doses (explained in the next section). Fig. 11 shows with increasing doses of γ -irradiation the increase in carbonyl group concentration in samples containing mixtures of stabilizers with comparison of systems with and without phenolic structure. The rate of increase in carbonyl group in mixture systems is lower than that of neat and single-stabilizer systems. It can be seen that addition of secondary HAS (C) to hindered phenol stabilizer X containing sample, has reduced the rate of increase in carbonyl group. Among the phenol systems, the samples of ternary mixture (CTXS) and CX have shown lower rate of increase i.e. oxidation. In phenol-free systems, the reduction in the rate of oxidation is observed and samples of CTS have shown higher stabilization efficiency in terms of reduction in carbonyl group evolution. Among all the mixtures, CTS and

CX have shown higher stability against for all the doses of γ -irradiation indicating the longer durability for longer period. It is also indicating that the phenolcontaining systems have shown longer period of stabilization than phenol free systems. The order of stabilization efficiency with increasing doses of γ -irradiation above 25 KGy is changed. This can also be attributed the consumption of stabilizers with increasing doses of γ -irradiation.

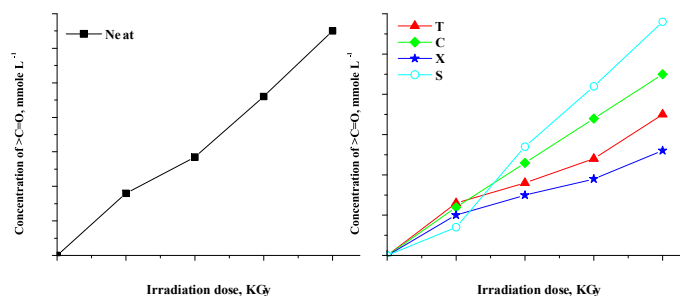


Fig. 10 Carbonyl group increase in neat and single-stabilizer systems

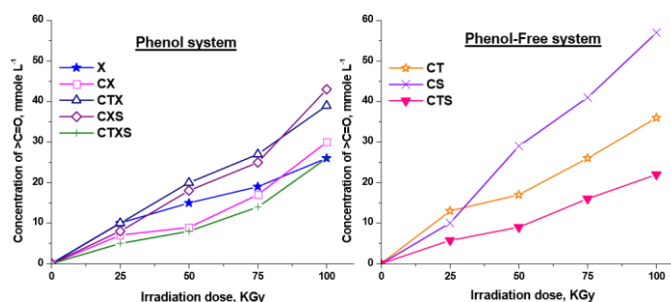


Fig. 11 Change in carbonyl group concentration of phenol and phenol-free systems upon γ -irradiation

D. Consumption of Stabilizers

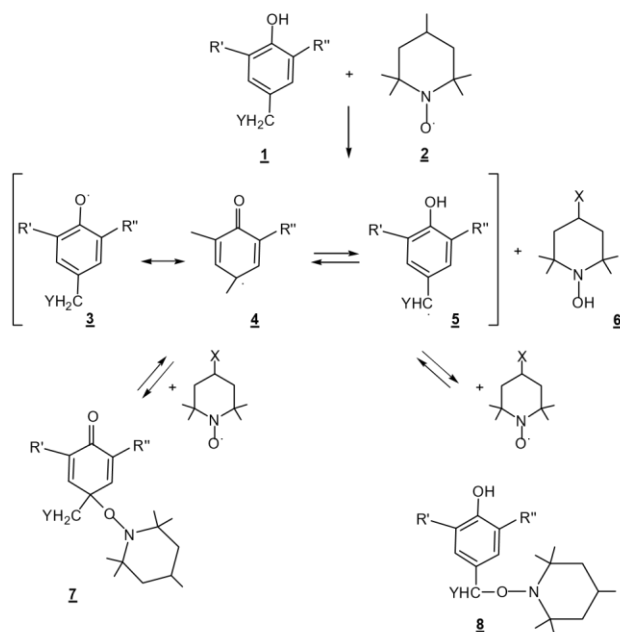
The change in the order of stabilization efficiency, in terms of reduction in the rate of carbonyl group evolution, can be attributed to the consumption of stabilizers. This may be in the form of physical loss of stabilizer from the samples (by evaporation, leaching etc. during processing and γ -irradiation) and/or transformations of active form stabilizer to inactive form during γ -irradiation. If one stabilizer is not affecting the stabilization mechanism of other stabilizer, the rate of carbonyl group evolution should not be changed or the order of stabilization efficiency of mixtures should not be altered. As it was observed in Fig. 10 for the sample of 'S', sudden increase in carbonyl group above γ -irradiation dose of 25 KGy, can be attributed the fact of the disappearance of Irgafos-168. This observation was already reported by [28] that Irgafos-168 was fastest to disappear from the samples. Contrarily, the hindered phenol 'X' sample has not shown significant increase in carbonyl group concentration. This can be attributed that consumption of hindered phenol 'X' is slower than others and / or lower rate of loss of hindered phenol in the film.

Among mixtures, higher protection ability of 'CX' was observed which can be attributed to the interaction of secondary HAS and hindered phenol. The retained concentration of Chimassorb-994 alone and with its blends was determined from

triazine absorption according to the method reported some were else [29]. Table III shows the retained concentration of Chimassorb-994 after sterilization to 25 KGy. It is seen that Chimassorb was extensively consumed when it used in combination with Tinuvin-765 (CT). This may explain the antagonistic effect of the CT mixture. However, it is highly preserved when it combined with Irgafos-168. The preservation of oligomeric HAS ‘C’ was observed not only with combination of ‘S’ and ‘C’ but also for ‘S’ with other systems as ‘CT and CX’ which is indication of the synergistic effect. These data reflected the suitability selection of different kinds of stabilizers and antioxidants to be combined with oligomeric HAS and its effectiveness.

TABLE III

Components	C	CT	CX	CS	CTX	CTS	CXS	CTXS
Chimassorb 994 retained (%)	68	21	57	87	nv	82	72	nv



THE RETAINED CONCENTRATION OF OLIGOMERIC HALS (CHIMASSORB-994)

AFTER GAMMA STERILIZATION

x

R'

YH₂C

x

x

Fig. 12 Possible interactions of hindered phenol and hindered amine

E. Synergism vs. Antagonism in Stabilization Efficiency

The results of changes in tensile property, i.e. elongation at break (%) have shown that the mixture of secondary HAS and tertiary HAS (radical scavengers) shows the antagonistic effect. Their combination with organo-phosphite stabilizer (hydroperoxide decomposer) i.e. CTS among all the samples has exhibited the stability against γ -irradiation in synergistic way. Among phenol system, the addition of secondary HAS ‘C’ to hindered phenol ‘X’ reduced the discoloration. Their combination with organo-phosphite ‘S’ has exhibited synergistic effect stabilization against discoloration in samples

CXS and CTXS as shown in Fig. 9. A complementary mechanism was recently proposed by [30] in which the effect of γ -irradiation on the oxidation of PP containing Irgafos-168 was studied and found that the conversion of the phosphite to the phosphate reflects the role of Irgafos-168 in reacting with peroxy radicals that are generated during γ -irradiation. By measuring carbonyl group concentration, which indicates oxidative degradation, it was observed that CT and CS have shown lower stability and CTS, CX and CTXS have exhibited higher stability. The combination of both secondary and tertiary HAS i.e. CT has shown antagonistic effect on oxidation with linear increase in carbonyl group concentration. The addition of hindered phenol ‘X’ to secondary phenol ‘C’ has shown higher and longer period stabilization against γ irradiation (up to 100 kG y) induced oxidation. This can be attributed to lowered consumption of ‘C’ by ‘X’. According to [31], [32], the interaction between hindered phenol and hindered amine may reduce the consumption of secondary HAS as shown in Fig. 12. The hindered phenol can react with nitroxyl radicals, which are generated from secondary HAS, to give hydroxylamines (6) and with phenoxyl radicals (or the mesomeric and tautomeric forms, 3-5) [15]. These compounds are, in turn, radical scavengers and add nitroxyl radicals to reaction products 7 and 8. It was reported [33] that the oxidative products of phenols, such as substituted benzoquinone, diphenoquinone, and stilbenequinone, enhanced the protective effect of HAS in photooxidation of heptan using stilbenequinone as a common model of oligomeric quinomethides. The direct recombination of free carbon radical species derived from oxidized phenols with $>NO\cdot$ was also observed [34], [35]. It is inferred from existing literature support [33], [36], [37] that

compounds like 7 were most likely decomposed into the respective quinomethide and >NOH compounds, or they could undergo a recombination to cyclohexandiennonyls and >NO• whereas, compounds like 8 or its analogs were obtained from phenolic antioxidants and various >NO•. According to the obtained results, the mixture of secondary and tertiary HAS (CT) has shown an antagonistic effect, whereas their combination with organo-phosphite i.e. CTS have shown a synergistic effect of stabilization even at higher doses of γ -irradiation. On the other hand, organo-phosphite 'S' alone shows better stabilization up to 25 kGy and at 50 kGy of γ -irradiation. The synergistic effect of stabilization in CTS and CTXS can be attributed to the reduced consumption of stabilizers. It was found [38] that during the processing of HDPE at 220°C in the absence of organo-phosphite stabilizer, as much as 45% of the phenolic antioxidant is consumed after one extrusion pass, whereas the presence of a phosphite stabilizer reduces the consumption of phenolic antioxidant to 20% after the first extrusion pass. Thus, the synergistic effect obtained by combination of organo-phosphite with hindered phenols and hindered amines could explain that organo-phosphite preserves the concentration of hindered phenols and replaces the hindered amines during polymer processing. Furthermore, rapid oxidation of the phosphites to phosphates by residual oxygen dissolved in the polymer may contribute to stabilization during processing [37].

IV. CONCLUSION

The stabilization of γ -sterilized ethylene-propylene-diene terpolymer was studied using mixtures of different stabilizers, which follow the different stabilization mechanism and are approved for food contact applications. It was observed that the stabilization efficiency in terms of tensile properties and discoloration of one stabilizer is being affected by another stabilizer. Among phenol containing systems where we mostly observed discoloration due to the oxidation of hindered phenol, the combination of secondary HAS, tertiary HAS, organo-phosphite and hindered phenol exhibited improved stabilization efficiency than single or binary additive systems. The mixture of sec- & tert- HASs, has shown antagonistic effect of stabilization whereas their combination with organophosphite has exhibited synergistic effect of stabilization even at higher doses of γ -irradiation. The combination of sec- & tert-HASs with peroxide decomposer reduced the consumption of stabilizer imparting stability against higher doses of γ -irradiation. In this study, we found that combinations of sec- & tert-HASs based primary antioxidants with organo-phosphite based hydroperoxide decomposers have (secondary antioxidants) exhibited synergistic effect of stabilization. Thus, it can be concluded that stability against γ sterilization can be improved by blends of different stabilizers, which protect via different mechanism at different stages synergistically and approved for food contact applications.

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