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Study of the effect of natural antioxidants in polyethylene: performance of β-carotene

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Abstract

The effect of β-carotene on the behaviour of polyethylene stabilized with α-tocopherol and a phosphonite antioxidant was studied under processing and storage conditions. The amount of β-carotene ranged between 0 and 2000 ppm. The polymer was characterised by different methods after processing then during and after storage at ambient temperature in light and dark. β-Carotene hinders the oxidation of polyethylene and does not increase the chain extension reactions during processing, though more vinyl groups and phosphonite molecules react. β-Carotene colours polyethylene strongly already at low concentrations. The reactions of the polymer and β-carotene are affected strongly by the storage conditions. The presence of β-carotene does not influence the stabilizing efficiency of the primary and secondary antioxidants. In dark the molecular structure of the polymer does not change appreciably, while the reactions of β-carotene lead to an increase in the yellowness index. In light the molecular characteristics of polyethylene undergo significant changes indicating long chain branching. The polymer fades rapidly after an induction period. The length of the induction period is not influenced by light. The rate of the degradation reactions of β-carotene during storage is controlled by its concentration and film thickness. Visible autoaccelerated decomposition in light renders β-carotene candidate as an indicator in active packaging materials.

Key words: polyethylene, stabilisation, natural antioxidant, α-tocopherol, β-carotene, phosphonite, active packaging

1. Introduction

Polyethylene is one of the main components of modern food packaging materials used for various purposes. This polymer is of low density, translucent, water-resistant, harmless for human health, recyclable, and cheap. However, polyethylene has to be protected against degradation which occurs as an effect of heat, shear, oxygen and/or UV light during processing and application. The degradation of polyethylene starts at the weak sites of the polymer chains (double bonds, branching points) with the formation of alkyl radicals which react rapidly with oxygen yielding peroxy radicals. These abstract hydrogen atoms from the polymer backbone and the hydroperoxide groups formed decompose fast to reactive oxy and hydroxyl radicals resulting in an auto-accelerated degradation process [1-5]. Comparing the effect of unsaturations on the thermal- and photo-oxidative stability of polyethylene revealed that the number of unsaturated groups affect significantly thermal oxidation, while their concentration does not influence the rate of photo-oxidation [6]. The degradation of polyethylene can be inhibited by antioxidants. Combinations of hindered phenols and phosphorous antioxidants are usually used as processing stabilisers. The phosphorous antioxidant inhibits degradation reactions by decomposing hydroperoxide groups to alcohols and it reacts also with carbon-centred, peroxy and oxy radicals [1,7,8]. Its efficiency is affected strongly by its chemical composition and thermal stability, as well as the amount of oxygen present [7-10]. Hindered phenols terminate autoxidation by trapping alkylperoxy, alkoxy and alkyl radicals [11-14]. The efficiency of the phenolic antioxidant depends on the number of hydroxyl groups and the nature of substituents at the orto and para positions to the phenolic OH group [15,16]. The synergistic effect of phenol/phosphorous antioxidant combinations compared to single antioxidants can be partly attributed to the reduced rate of consumption of each type of stabiliser during the processing of polyethylene [10].

Different synthetic antioxidants are used for stabilisation in practice. The stabilisation of polyethylene with natural antioxidants for packaging materials is a new challenge both from the scientific and the industrial point of view. Replacing synthetic phenolic antioxidants by them could stop worries caused by the possible harmful effects of their reaction products on human health [17]. Active packaging films can be produced by incorporating natural antioxidants into the polymer matrix resulting in quality improvement in different ways. Some examples: 1) The shelf-life of oxygen-sensitive products can be prolonged by using radical scavenging natural antioxidants [18-21]. 2) The migration of antioxidants (like vitamins, flavonoids) from the packaging material to the packaged goods may be also beneficial. 3) Most of the natural antioxidants are colourful substances. Intelligent packaging materials may be produced with their application, as the loss in colour can indicate the expiration of guarantee for the product.

β-Carotene is one of the colourful carotinoids with antioxidant activity. It is a strongly-coloured red-orange pigment present in many plants and fruits, like carrots, pumpkins, or sweet potatoes. β-Carotene is the pro-vitamin of vitamin A and is widely used as a colorant in foods and beverages. It is a non-polar highly conjugated lipophilic hydrocarbon compound (Table 1). The eleven conjugated C=C double bonds serve as a chromophore moiety in the molecule, which is responsible for the light absorption and the colour of β-carotene [22]. Accordingly, β-carotene has a characteristic UV-VIS spectrum, in which the position of the principal absorption maximum (λ_{max}) depends on the configuration [23,24] and oxidation of the molecule [25,26], as well as on the type of the solvent used [25,27] according to the changes in transition energies between the ground and excited states.

The melting point of β-carotene is higher than 180 °C, but melting is not reversible and the true melting point cannot be determined [25]. Pure crystalline β-carotene (purified by fractional dissolution) is black but undergoes fast direct oxidation by air in the crystal phase even at low temperatures (-80 °C) in dark. Oxidation results in a change of colour to orange or red, the powder becomes similar in appearance and composition to laboratory samples available commercially [25]. The oxidation of β-carotene with molecular oxygen is an autocatalytic free radical process which leads to the formation of different epoxycarotenoids, apocarotenals, small molecular mass products, and some oligomeric/polymeric materials, some of them representing the key aroma compounds in certain flowers, vegetables, and fruits [28-33]. The initial site of the oxygen attack on the β-carotene molecule occurs at the terminal double bonds resulting in predominant formation of epoxides [30,34]. These and long chain β-apocrotenals formed in the first stage of oxidation decompose to lower molecular mass carbonyl-containing compounds in further oxidation reactions [30]. The pathway of cleavage of the molecule (central or random) is affected by the surrounding medium (type of solvent), as well as the absence or presence of a phenolic antioxidant [35]. Phenolic antioxidants, like BHT and α-tocopherol, inhibit the oxidation of β-carotene [30,35]. β-Carotene is more resistant to heat than to oxygen [36,37]. Besides isomerisation of *cis*- to *trans*-isomer, a few high molecular mass components are formed at high temperatures in nitrogen atmosphere, while polymerisation and decomposition reactions take place simultaneously in air [28,36]. As an effect of UV irradiation the C=C and C-C bonds of the hydrocarbon chain break leading to a loss of colour [22]. The UV stability of β-carotene can be improved by the addition of a photostabiliser which absorbs light below 465 nm [22,38].

β-Carotene is considered as a chain-breaking antioxidant, as it exhibits high reactivity towards carbon-centred, peroxy, alkoxy, and NO_2 radicals [39]. It can even prevent the photosensitisation of human skin [40]. According to Ozhogina and Kasaikina [31] β-carotene reacts primarily by the addition of free radicals to its conjugated system. The radical-trapping behaviour of β-carotene depends on the partial pressure of oxygen [41,42]. It proved to be a good radical-trapping antioxidant at partial pressures lower than the pressure of oxygen in normal air. At higher oxygen pressures, β-carotene loses its antioxidant activity and shows an autocatalytic, prooxidant effect, particularly at relatively high concentrations. The mixtures of β-carotene, α-tocopherol, and ascorbic acid provide better protection against protein oxidation than any of the components alone [42,43].

Although the antioxidant activity of β-carotene has been investigated mainly in food and medical sciences, some experiments have already been carried out also in polymeric materials. Abdel-Razik [44] found that β-carotene increases the thermo-oxidative stability of ABS copolymer and explained the effect by the formation of biradicals which react rapidly with oxygen molecules inhibiting the formation of alkoxy and peroxy radicals from the polymer. López-Rubio and Lagaron [45] observed the UV stabilising effect of β-carotene in biopolyesters [poly(lactic acid), polycaprolactone, and polyhydroxybutyrate-co-valerate]. β-carotene plasticise these biopolymers already at small concentrations (0.4 w/w %) and a part of the effect is retained even after UV-VIS irradiation.

Preliminary experiments run in our laboratory revealed that β-carotene improves the processing stability of polyethylene. The positive effect is further enhanced by the addition of a phosphonite secondary antioxidant; the efficiency of this additive combination proved to be similar to that of the synthetic phenolic antioxidant package frequently used in industrial practice [46]. Gradual loss of the original orange colour of films stored in an artificially lighted room was observed in the experiment, which was attributed to the decomposition of β-carotene. As α-tocopherol inhibits oxidation of β-carotene [30,35], and a phosphonite antioxidant enhances its stabilising efficiency [46], the effect of β-carotene on the characteristics of polyethylene was investigated in the presence of these additives in this work. Two main questions were studied: 1) the effect of the concentration of β-carotene on the processing stability of polyethylene; 2) changes in polymer characteristics during storage at ambient temperature.

2. Experimental

The experiments were carried out with the Tipelin FS 471 grade ethylene/1-hexene additive-free copolymer powder of Tisza Chemical Group Ltd. (*TVK*) (PE; melt flow index of the powder: 0.32 g/10 min, nominal density: 0.947 g/cm^3) polymerized with a Phillips catalyst. The polymer was stabilised with 500 ppm α-tocopherol (Ronotec 201; *Hoffmann-La Roche*), 2000 ppm phosphonite antioxidant (Sandostab P-EPQ; *Clariant*), and different amounts of β-carotene (purum, ≥97 %, UV, *Sigma*) ranging from 0 to 2000 ppm.

The polymer powder was homogenised with the additives in two steps. α-tocopherol dissolved in acetone and the phosphonite antioxidant was added gradually to the polymer powder under mixing at a rate of 500 rpm for 10 min in a high-speed mixer (Henschel FM/A10). The blend was dried at ambient temperature and after the evaporation of acetone β-carotene was mixed to it under the same conditions as previously. Subsequently the powder was extruded and pelletised using a Rheomex S 3/4" 25 L/D single screw extruder attached to a HAAKE Rheocord EU 10 V driving unit at a rate of 50 rpm and barrel temperatures of 180, 190, 190, and 190 °C. Plates of 1 mm and films of 100 μm thickness were compression moulded from the pellets using a Fontijne SRA 100 equipment.

The chemical structure of the polymer and the concentration of the phosphonite stabiliser were determined by Fourier transformed infrared (FT-IR) spectroscopy (Tensor 27, *Bruker*). Five parallel measurements were carried out in each case. The spectrum of the nascent polymer powder was recorded by Diffuse Reflectance Fourier Transform Infrared (DRIFT) spectorscopy [47]. The concentration of the residual phosphonite and that of the vinyl and carbonyl groups in the processed polyethylene were determined from the absorbance spectra of compression-moulded films [9]. The UV-VIS spectra of 100 μm thick films were recorded in the wavelength range of 200-600 nm using a Unicam UV 500 type spectrophotometer. The absorption spectra are complex, as showed by Fig. 1. The absorption band between 200 and

300 nm can be assigned mainly to α-tocopherol, although β-carotene dissolved in cyclohexane has also a small band in this region. The main absorption band of β-carotene is located between 400 and 600 nm (blue-green region), and the band between 300 and 400 nm originates also from β-carotene; it is the *cis*-band region [23,24]. The concentration of residual β-carotene in polyethylene films was calculated from the absorption intensity at 456 nm after calibration in cyclohexane solutions. This method yields approximate values for the concentration of β-carotene in polyethylene due to the effect of different factors (e.g., isomerisation, oxidation) on the UV-VIS spectra. The colour of the samples was measured with a Hunterlab Colourquest 45/0 apparatus on 1 mm thick plates and the yellowness index (YI) was used for characterisation. The UV-VIS spectra and YI were measured after processing, and after aging the samples at ambient temperature in a container placed in a chest of drawers (in dark) and in the window of a room illuminated by natural light (in light) for different lengths of times. The melt flow index (MFI) of the samples was determined according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D tester running five parallel measurements. The residual thermo-oxidative stability of the polymer was characterised by the oxidation induction time (OIT) measured in a Perkin Elmer DSC-2 apparatus at 200 °C in oxygen flow.

2. Results and discussion

2.1. Processing stability

The polymer and the additives participate in different chemical reactions during the processing of polyethylene. These reactions are influenced significantly by the antioxidant combination and the initial concentration of β-carotene. Without any antioxidant the vinyl content of the nascent polymer powder drops from 0.91 to 0.66 vinyl/1000 C after processing. The protecting effect of the α-tocopherol/phosphonite antioxidant pair is well reflected in the reduced change to 0.88 vinyl/1000 C at 0 ppm β-carotene. With the addition of β-carotene to the antioxidant package the concentration of vinyl groups decreases slightly reaching a value of 0.84 vinyl/1000 C at 2000 ppm β-carotene concentration. The residual concentration of phosphonite antioxidant decreases, as well. Similarly to our earlier studies on polyethylene stabilisation [10], the number of vinyl groups changes linearly with the residual amount of phosphonite. β-Carotene also participates in the chemical reactions taking place during the processing of polyethylene. The loss in β-carotene derived from the absorption intensities at 456 nm in the UV-VIS spectra (Fig. 1) increases linearly with its initial concentration and it is around 50-60 wt % at each additive package. Figure 2 shows that the reactions of vinyl groups and phosphonite are directly related to those of β-carotene.

The melt flow index of the nascent polymer powder (0.32 g/10 min) decreases to 0.13 – 0.14 g/10 min independently of the β-carotene content after processing (Fig. 3). This is a smaller change than without any stabiliser where MFI drops to 0.06 g/10 min. The independence of MFI from β-carotene concentration indicates that the reactions of vinyl groups do not always lead to the chain extension of the polymer, though the latter is characteristic for the degradation of Phillips type polyethylenes [10]. This can be attributed to the radical trapping ability of β-carotene at low oxygen concentrations [31,41,42]. β-carotene protects the polymer from oxidation during processing. In the absence of β-carotene the polymer oxidises slightly (0.042 mmol C=O/mol PE), but carbonyl groups are not formed when the concentration of reacted β-carotene is ≥200 ppm. These results can be explained by the reactivity of β-carotene towards oxygen and different radicals (carbon-centred, oxy) [30,31,39]. β-Carotene reacts fast with molecular oxygen present in small concentrations in the extruder and hinders the formation of peroxy macroradicals which are the precursors of oxidised derivatives. The reactivity of β-carotene towards oxygen leads to an opposite effect at high oxygen concentrations. The OIT measured at 200 °C in pure oxygen atmosphere decreases with increasing concentration of unreacted β-carotene (Fig. 4), which confirms that β-carotene looses its antioxidant activity and has a prooxidant effect at large oxygen concentrations [41,42].

β-carotene colours polyethylene already at small concentrations due to its eleven conjugated C=C double bonds absorbing light in the blue-green region. Although the absorption intensity at 456 nm increases linearly with the amount of β-carotene added to the polymer (Fig. 1), the yellowness index determined from the colour coordinates changes non-linearly (Fig. 5a). 250 ppm β-carotene increases the yellowness index from 2.5 to 135 and turns the visible colour from colourless to orange-yellow. With further addition of β-carotene the colour deepens gradually and turns from orange-yellow to red-orange (Fig. 5b). At the same time yellowness index increases more moderately and reaches a value of YI = 175 at a β-carotene concentration of 2000 ppm. This character of the yellowness index indicates limited solubility of β-carotene in polyethylene. From the concentration dependence of YI we can deduce that the solubility is below 200 ppm.

Summarising the results we can conclude that β-carotene in combination with α-tocopherol and phosphonite antioxidants inhibits the oxidation of polyethylene, does not affect its melt flow index, increases the number of phosphorous stabiliser molecules participating in chemical reactions and colours the polymer to orange during processing.

2.2. Storage at ambient temperature

The film and sheet samples were stored at ambient temperature in dark and in light for various lengths of times. UV-VIS spectra and yellowness index were measured regularly as a function of storage time.

Some of the UV-VIS spectra taken from the film (100 μm thick) containing 1500 ppm β-carotene stored in dark for different times are shown in Fig. 6. In the first period (8 days) isomerisation of β-carotene is revealed by the decrease in the intensity of the absorption band between 300 and 400 nm (characteristic of the *cis*-isomer) and the increase of the one appearing between 400 and 600 nm. The maximum of the main band shifts from 456 nm to 460 nm. This introduces some uncertainties in the determination of the concentrations of β-carotene from the UV-VIS spectra but deviations do not exceed 10 %. In the further period of storage in dark slow loss in the β-carotene concentration occurs which is less than 150 ppm after 133 days. The occurrence of some reactions of α-tocopherol is indicated by the increase in the intensity of the absorption between 250 and 300 nm and the shift of the peak maximum from 272 nm to 270 nm.

The yellowness index values of 1 mm thick plates stored in dark are shown as a function of time in Fig. 7. An increase of YI can be observed even for the sample stabilised with α-tocopherol/phosphonite antioxidant combination without β-carotene. In this latter case yellowing of polyethylene can be explained by the reactions of α-tocopherol, as its transformation products are more coloured than the parent antioxidant [48]. YI values of the polymer processed with β-carotene increase sigmoidally with storage time indicating autocatalytic reactions. The time elapsed before the start of accelerated change in YI (induction time) increases with increasing residual concentration of β-carotene measured after processing (Fig. 8). The differences in YI measured before and after storage in dark for 182 days are ΔYI ≈ 25-30 at β-carotene concentrations below 600 ppm and decrease at higher β-carotene contents. The shift of the main UV-VIS absorption peak of β-carotene to higher wavelengths and the increase in YI can be attributed to the reaction of β-carotene with oxygen. As the terminal double bounds of β-carotene are less stable than the central one (because of resonance) [49] and the C-H bond is the weakest at the α-position next to the double bond [50], we may assume that the oxidation starts there. One or two peroxy radicals then hydroperoxide groups are formed which participate in further reactions. The reaction products formed in dark do not contain carbonyl groups. The changes in colour characteristics confirm that the reactions take place in the terminal rings of the molecule and may originate from an increase in the number of conjugated double bounds in the reaction products or from a decrease in solubility and separation of reacted molecules from the solution state. The decrease in ΔYI with increasing concentration of β-carotene above 600 ppm suggests higher probability of the latter case. Further experiments are in progress to explore the mechanism of reactions in dark.

The chemical structure and the melt flow properties of the polymer do not change significantly during storage in dark for 8 months. Although vinyl groups participate in some reactions resulting in a slight decrease in their concentration ($-\Delta c_{vinyl}$= 0.03-0.07 vinyl/1000 C) but the polymer does not oxidise and its melt flow index remains practically constant (ΔMFI=0.01 g/10 min). From these results we can conclude that the reactions of additives leading to some deepening of colour during storage in dark do not affect the stabilising efficiency of antioxidants which controls the characteristics of polyethylene.

The degradation of β-carotene in light is fast, occurs heterogeneously, and results in fading of polyethylene. The time of the complete loss of colour depends on the concentration of β-carotene and the thickness of the sample. Fig. 9 shows some UV-VIS spectra of 100 μm thick films processed with 1500 ppm β-carotene and stored in light at ambient temperature for different times. First (8 days of storage) isomerisation of β-carotene occurs revealed by the decrease in the intensity of the absorption band in the region of 300-400 nm (*cis*-isomer) and the increase of the band appearing between 400 and 600 nm. The maximum of the main absorption band shifts from 456 nm to 460 nm and then to 462 nm during further storage. Fast decomposition of β-carotene is revealed by the decrease and finally the complete disappearance of the absorption band between 300 and 600 nm in 25 days. The maximum of the absorption band of α-tocopherol shifts gradually from 272 nm to 267 nm indicating its participation in chemical reactions. The concentration of β-carotene determined from the intensity of the main absorption peak is plotted as a function of storage time in Fig. 10. We can see that the reactions of β-carotene are autoaccelerated and the increase in the initial concentration results in an increase of decomposition rate. Changes in the yellowness index of 1 mm thick plates confirm the autoaccelerated nature of β-carotene decomposition in light (Fig. 11). YI of the polymer stabilised with α-tocopherol/phosphonite antioxidants increases gradually as a function of storage time due to the reactions of α-tocopherol. In the presence of β-carotene, following an induction time the yellowness index drops unexpectedly fast and almost independently of the concentration of β-carotene to a value corresponding to the polymer processed without this additive. Two points must be emphasised here. The length of the induction period, as well as the overall decomposition time of β-carotene do not depend only on its concentration measured before storage but also on the thickness of the polymer sample. The time of complete decomposition of β-carotene in light is around 30 days in 100 μm thick films independently of the initial concentration (Fig. 10), while it changes from 80 to 170 days with increasing initial concentration in 1 mm thick plates (Fig. 11). It is also remarkable, that the length of the induction time of YI is similar in dark and light as shown in Fig. 8. This reveals that the reactions of β-carotene are governed primarily by the composition of the additive package and the thickness of the sample, and depend less on the presence of light in the induction period. As we deduced above, peroxy radicals and hydroperoxide groups in the allylic position to the terminal double bonds can be expected to form in the induction period of oxidation. In this stage the rate of oxidation must be determined primarily by the concentration of oxygen which decreases with increasing film thickness, i.e., with the decrease in the surface/volume ratio. The eleven conjugated double bonds of β-carotene absorb a part of visible light and get into excited state. In this state the molecule becomes more sensitive to oxygen attack. After the induction period the rate of oxygen uptake accelerates and decomposition becomes the main direction of degradation in light.

The radiation of light does not influence only the reactions of the additives but also the characteristics of polyethylene measured after storage for 8 month. The concentration of vinyl groups decreases more ($-\Delta c_{vinyl}$= 0.12-0.14 vinyl/1000 C) than in dark and melt flow index decreases significantly (ΔMFI = –0.11 g/10 min) independently of the concentration of β-carotene. This change can be attributed to the reactions of vinyl groups leading to extension of polymer chains after total consumption of the phosphorous antioxidant. Carbonyl groups form, their concentration increases with β-carotene content. Fig. 12 reveals that the formation of carbonyl groups is accompanied by a decrease in the number of vinyl groups participating in reactions. This and the independence of MFI from the concentration of β-carotene indicate that β-carotene oxidises primarily and protects the polymer from degradation in some extent.

We can conclude that storage in light results in reactions of the unsaturated groups of polyethylene leading to long chain branching. After an induction time β-carotene decomposes in oxidation processes which protect the polymer from degradation in some extent and result in fast fading of polyethylene.

3. Conclusions

Studies of the effect of β-carotene in polyethylene stabilised with a combination of α-tocopherol and phosphonite reveals that the additive with its eleven conjugated double bonds colours the polymer significantly but does not reduce the stabilizing efficiency of antioxidants either during processing or in the course of storage at ambient temperature. β-Carotene reacts with molecular oxygen both at high and ambient temperatures. It hinders the oxidation of polyethylene completely under the processing conditions which cannot be avoided with the usually applied phenolic/phosphorous antioxidant packages. The direction of reactions of β-carotene at ambient temperature is controlled by the absence or presence of light, as well as the concentration of oxygen. The molecular structure of polyethylene is primarily determined by the stabilizing efficiency of antioxidants and is not affected significantly by the reactions of β-carotene during storage at ambient temperature. The colour of the polymer depends on the nature of the reaction products of β-carotene. Deepening of orange colour occurs in dark, while the polymer fades rapidly in light after an induction period. This special character of colour changes could be utilised in developing functional packaging materials with indicator function.

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Table 1

Chemical composition of the antioxidants studied

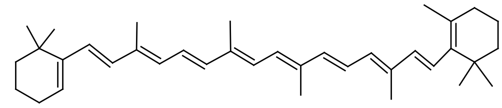
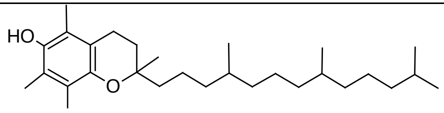
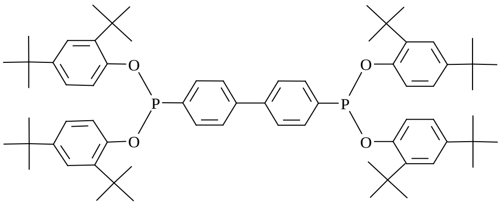
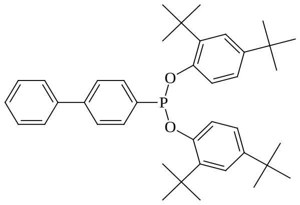
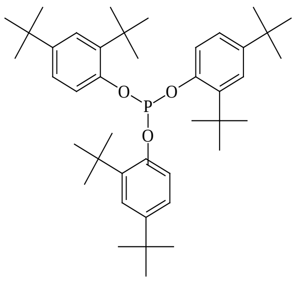
Commercial name	Chemical composition	Molecular mass (g/mol)
β-carotene		537
α-tocopherol		431
Sandostab P-EPQ *Diphosphonite* >70%		1035
Monophosphonite ~20%		595
Phosphite <10%		647

Figure captions

Fig. 1 UV-VIS absorbance spectra of polyethylene processed with α-tocopherol/phosphonite antioxidant package and β-carotene of 0 (—), 250 (– –), 500 (····), 1000 (··–··), 1500 (----), and 2000 (–·–) ppm. Absorption intensities are related to 100 μm film thickness.

Fig. 2 Effect of the reactions of β-carotene on the consumption of phosphonite antioxidant (●) and the decrease in the vinyl group concentration of polyethylene (■) during processing at 190 °C.

Fig. 3 Correlation between the vinyl group concentration and the melt flow index of polyethylene before and after processing with additive packages containing α-tocopherol/phosphonite antioxidant package and different amounts of β-carotene.

Fig. 4 Correlation between the residual concentration of β-carotene after processing and the thermo-oxidative stability of polyethylene measured at 200 °C in oxygen.

Fig. 5 Effect of the concentration of β-carotene on the colour of polyethylene pellets stabilised with α-tocopherol/phosphonite antioxidant combination; a) yellowness index, b) visual colour.

Fig. 6 UV-VIS spectra of polyethylene films of 100 μm thickness stabilised with 500 ppm α-tocopherol + 2000 ppm phosphonite + 1500 ppm β-carotene stored at ambient temperature in dark for 0 (—), 8 (– –), 20 (–·–), and 64 (–··) days.

Fig. 7 Discoloration of 1 mm thick polyethylene sheets processed with α-tocopherol/ phosphonite antioxidant package and β-carotene of 0 (∗), 250 (◇), 500 (△), 1000 (○), 1500 (∇), and 2000 (□) ppm during storage at ambient temperature in dark.

Fig. 8 Effect of the concentration of β-carotene on the time elapsing before accelerated change in the yellowness index (induction time) of 1 mm thick polyethylene plates stored at ambient temperature in dark (▲) and light (■).

Fig. 9 UV-VIS spectra of 100 μm thick polyethylene films processed with α-tocopherol/ phosphonite antioxidant package and 1500 ppm β-carotene stored at ambient temperature in light for 0 (—), 8 (– –), 15 (··–··), 20 (····), 22 (----), and 25 (–·–) days.

Fig. 10 Residual concentration of β-carotene in 100 μm thick polyethylene films processed with α-tocopherol/phosphonite antioxidant package and β-carotene of 250 (◆), 500 (▲), 1000 (●), 1500 (▼), and 2000 (■) ppm, stored at ambient temperature in light.

Fig. 11 Yellowness index of 1 mm thick polyethylene plates processed with α-tocopherol/phosphonite antioxidant package and β-carotene of 0 (∗), 250 (◇), 500 (Δ), 1000 (○), 1500 (∇), and 2000 (□) ppm, stored at ambient temperature in light.

Fig. 12 Correlation between the concentration of reacted vinyl groups and carbonyl groups formed in polyethylene processed with α-tocopherol/phosphonite/β-carotene additive packages and stored in light for 8 months.

Fig. 1

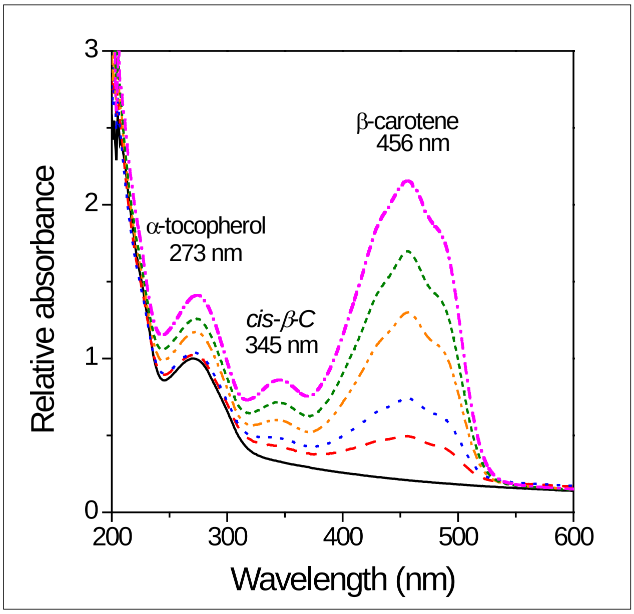

3
2
1
0
Relative absorbance
200
300
400
500
600
Wavelength (nm)
α-tocopherol
273 nm
cis-β-C
345 nm
β-carotene
456 nm

Fig. 2

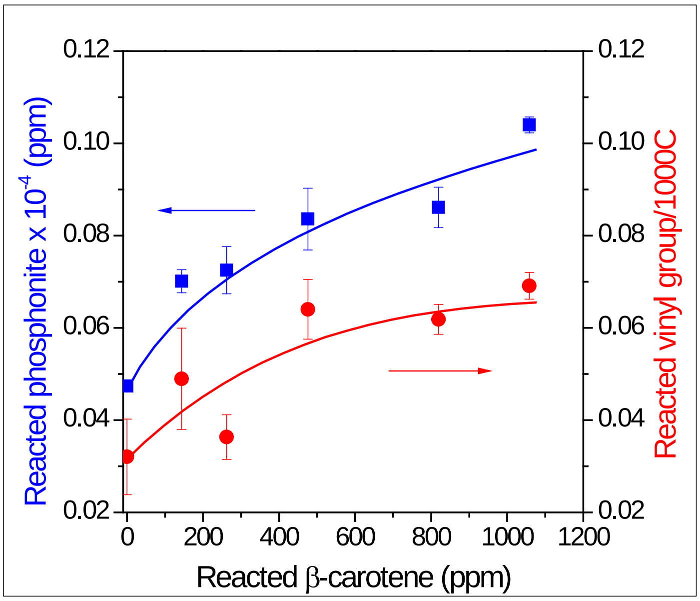

Reacted phosphonite x 10^{-4} (ppm)
Reacted vinyl group/1000C
Reacted β-carotene (ppm)
0.12
0.10
0.08
0.06
0.04
0.02
0
200
400
600
800
1000
1200

Fig. 3

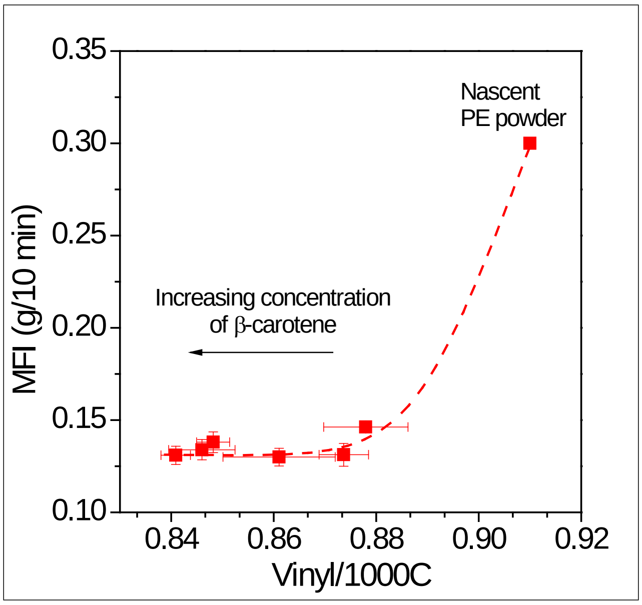

0.35
0.30
0.25
0.20
0.15
0.10
MFI (g/10 min)
0.84
0.86
0.88
0.90
0.92
Vinyl/1000C
Nascent
PE powder
Increasing concentration
of β-carotene

Fig. 4

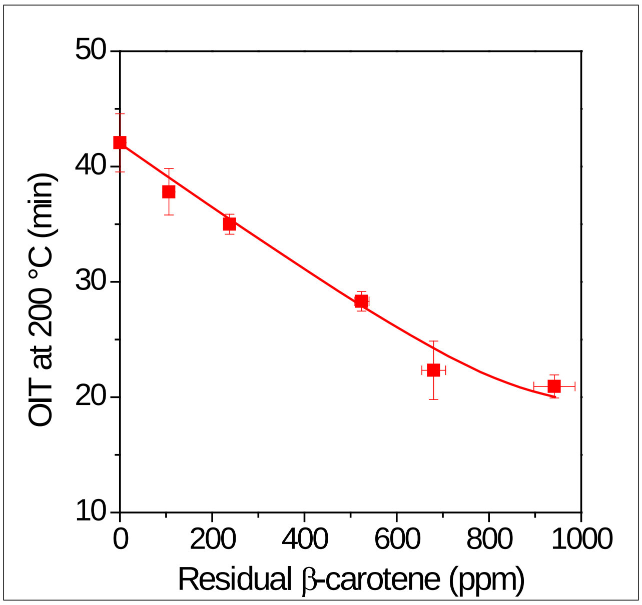

OIT at 200 °C (min)
50
40
30
20
10
0
200
400
600
800
1000
Residual β-carotene (ppm)

Fig. 5a

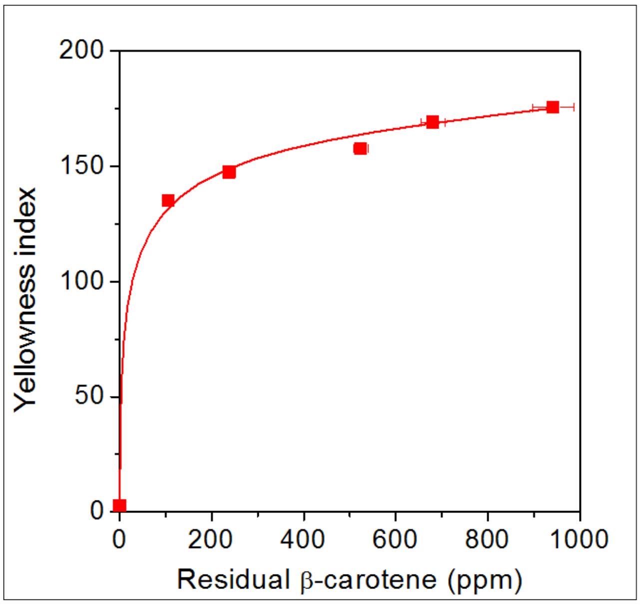

200
150
100
50
0
Yellowness index
0
200
400
600
800
1000
Residual β-carotene (ppm)

Fig. 5b

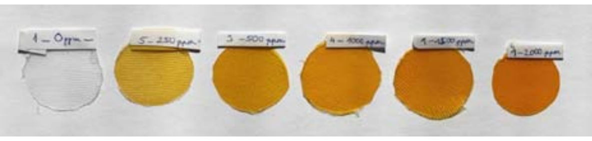

1 – 0ppm –
5 – 250 ppm
3 – 500 ppm
4 – 1000 ppm
1 – 1500 ppm
7 – 2000 ppm

Fig. 6

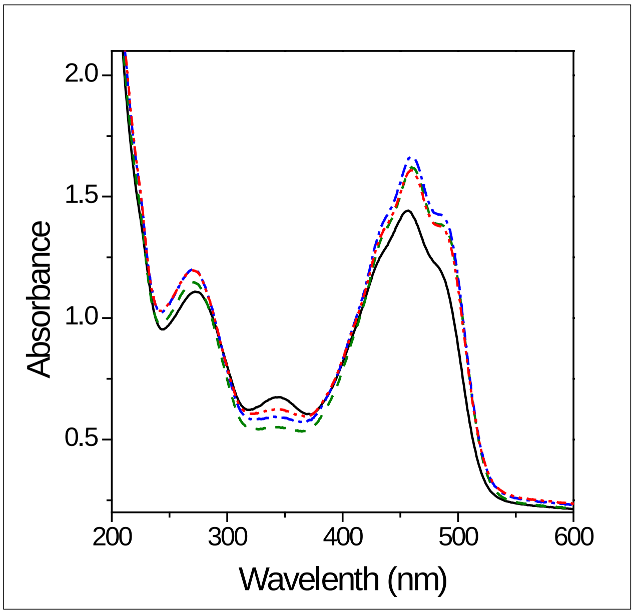


Fig. 7

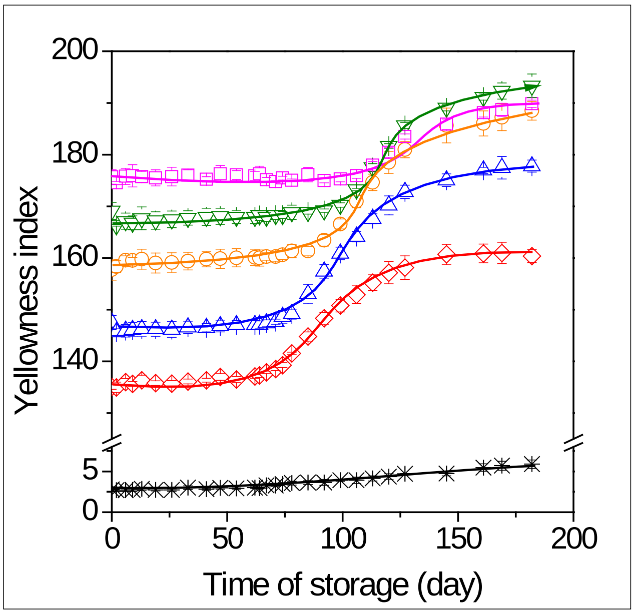
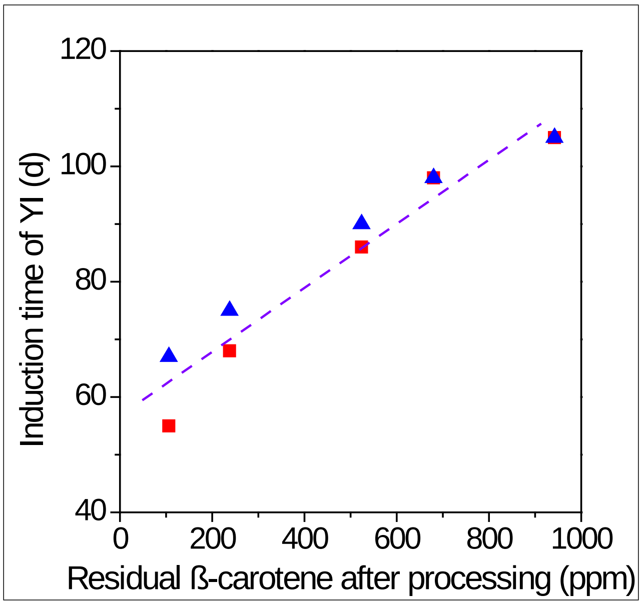

200
180
160
140
5
0
0
50
100
150
200
Yellowness index
Time of storage (day)

Fig. 8



120
100
80
60
40
0
200
400
600
800
1000
Induction time of YI (d)
Residual ß-carotene after processing (ppm)

Fig. 9

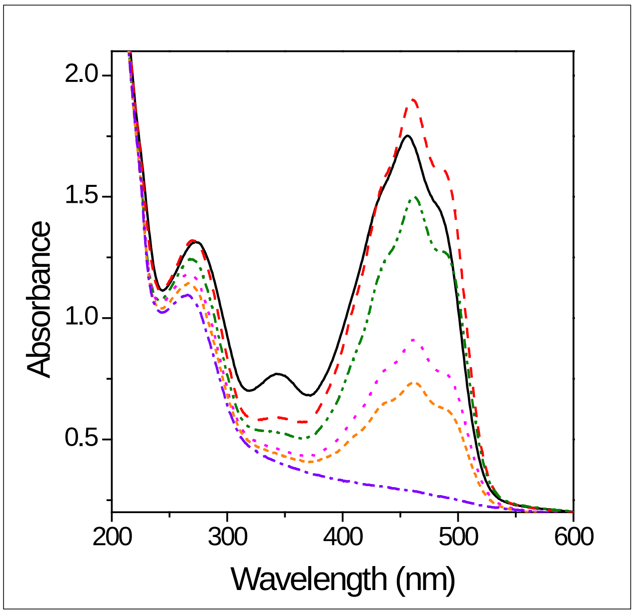


Fig. 10

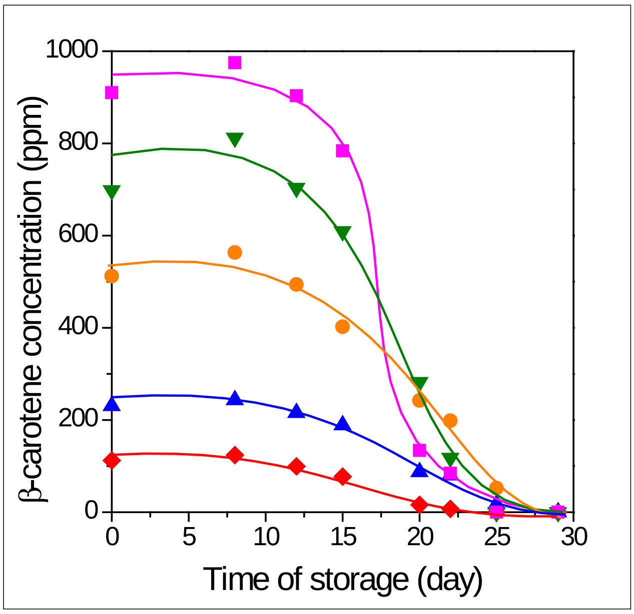

β-carotene concentration (ppm)
1000
800
600
400
200
0
0
5
10
15
20
25
30
Time of storage (day)

Fig. 11

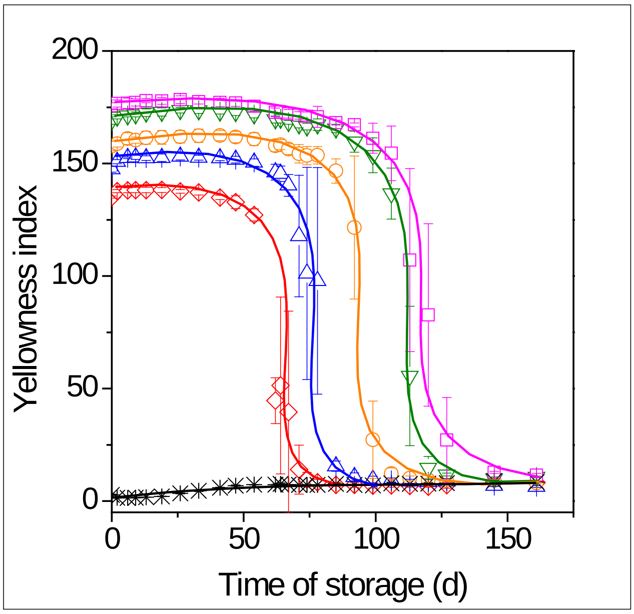
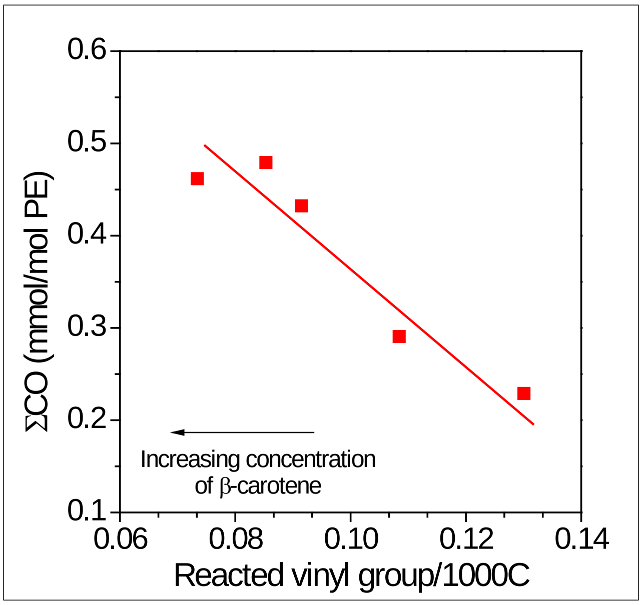

200
150
100
50
0
Yellowness index
0
50
100
150
Time of storage (d)

Fig. 12


0.6
0.5
0.4
0.3
0.2
0.1
ΣCO (mmol/mol PE)
0.06
0.08
0.10
0.12
0.14
Reacted vinyl group/1000C
Increasing concentration
of β-carotene