

Application of β -carotene, a Natural Flavonoid Dye, to Polymeric Materials as a Natural Antioxidant and Determination of Its Characteristics Using Cyclic Voltammetry and FTIR Spectroscopy

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The electrochemical oxidation of β -carotene was investigated at a Pt electrode using CV and DPV voltammetry methods. The electrooxidation of β -carotene is a diffusion-controlled, irreversible reaction. The effects of the scan rate on the electrode reactions and the parameters for the electro-oxidation of the substrate were determined. The obtained results confirm the exchange of two electrons during the first step followed by a chemical reaction, indicating that the electro-oxidation of β -carotene occurs according to the EC mechanism. A possible mechanism for the electrooxidation of β -carotene was proposed. The effect of β -carotene on stabilising composites consisting of a thermoplastic copolymer of ethylene and norbornene (Topas E-140), was also investigated. The addition of this natural pigment improved the resistance of the Topas material to the effects of climatic conditions, such as UV radiation, elevated temperature and humidity. Additionally, β -carotene served the role as an index of the ageing time.

Keywords: β -carotene; electrochemical oxidation; FTIR spectroscopy; thermo-gravimetric analysis

1. INTRODUCTION

Plant-derived natural dyes are easily extracted, completely biodegradable, and readily available. Many natural dyes, including carotene, cyanine, tannin, anthocyanin and chlorophyll, have been studied [1]. Carotenoids are a class of natural pigments that are primarily found in fruits and vegetables, and they typically possess 40 carbon molecules and multiple conjugated double bonds [2].

Carotenoids, which are responsible for the colouration of many plants and fruits, possess antioxidant activity due to their reactivity with singlet oxygen and oxygen free radicals [3]. As important nutrients, carotenoids may help to delay or prevent oxidative damage and offer protection against cancer, cardiovascular disease, eye diseases, atherosclerosis, and the aging process. [4,5]. Because of their various functions and interesting properties, carotenoids have become a fascinating field for interdisciplinary research in chemistry, biochemistry, medicine, biology, and other branches of science [6-8]. Carotenoids are not only natural antioxidants but also pigments in polymers, imparting polymers with features of pro-ecological materials [9, 10]. In our study, we propose polymeric materials that incorporate carotenoids.

β -carotene is one of the most studied carotenes (Fig. 1). This important nutrient is lipid soluble and is responsible for the colour of a wide variety of foods [11]. β -carotene is a natural dye that consists of a polyene system with 11 conjugated double bonds and a β -ring at each end of the chain [12,13]. It is one of the most effective vitamin A precursors, and it also prevents cancer and heart diseases [14]. Furthermore, β -carotene is a very important compound in photosynthesis, pharmacy, and medicine because of its antioxidant and free radical scavenging functions. β -carotene is a symmetric molecule that can generate different isomers because of its eleven conjugated double bonds [15, 16]. Thus, a simple and accurate method for detecting and studying β -carotene is very important. Methods for the determination of β -carotene have been developed by many researchers. To date, many methods for the determination of β -carotene have been described, including spectrophotometry and EPR [16-22], high-performance liquid chromatography [23-25], fluorescence [26], and chemiluminescence [27].

However, electro-analytical methods for the detection and determination of organic compounds in different media have recently attracted attention. Due to their high sensitivity and selectivity, voltammetric methods have been successfully used to investigate the redox behaviour of various compounds. These methods are relatively simple and very accurate [28-30]. The half-wave potential ($E_{1/2}$) is a useful parameter that provides information about the antioxidant activity of the compound under study [30, 31]. The electrochemical properties of β -carotene have been described in previous studies [3, 32-35].

The aim of this study was to determine the electrochemical behaviour of β -carotene at a platinum electrode during electrooxidation in non-aqueous media. Structural investigations of this compound were conducted using FTIR spectroscopy and thermogravimetric analysis. Furthermore, the addition of β -carotene to polymeric materials was investigated.

2. EXPERIMENTAL

2.1. Chemicals

Pure β -carotene (1,3,3-trimethyl-2-[3,7,12,16-tetramethyl-18-(2,6,6-trimethylcyclohex-1-en-1-yl)octadeca-1,3,5,7,9,11,13,15,17-nonaen-1-yl]cyclohex-1-ene, $C_{40}H_{56}$) was obtained from a commercial source (Sigma-Aldrich, Germany) and used as received.

The chemical used to prepare the β -carotene solutions was acetonitrile (CH_3CN) (pure p.a., POCh Gliwice, Poland), and tetrabutylammonium perchlorate ($(\text{C}_4\text{H}_9)_4\text{NClO}_4$) (Fluka, Germany) was used as a supporting electrolyte. The concentration of β -carotene was $5 \times 10^{-4} \text{ mol L}^{-1}$. All reagents used were of analytical grade.

2.2. Measurement methods

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV), was performed with a Autolab controlled by GPES software, version 4.8 (EcoChemie, The Netherlands). A three-electrode system was used for the measurements. Platinum was used as the anode and auxiliary electrode. The electrode potential was measured against a ferricinium/ferrocene reference electrode (Fc^+/Fc). All of the solutions were degassed with argon prior to the measurements. During the measurements, an argon blanket was maintained over the solution. The effect of the scan rate on the electro-oxidation of β -carotene in nonaqueous medium was assessed. Before measurements, the solutions were purged with argon to remove any dissolved oxygen. During the measurements, an argon blanket was kept over the solutions. All of the experiments were performed at room temperature.

FTIR analysis. IR spectra were recorded within the wavelength range of $3000\text{--}700 \text{ cm}^{-1}$ using a Nicolet 6700 FTIR (Thermo Scientific). The measurement parameters were as follows: 128 scans, 8 cm^{-1} resolution, and a DTGS/KBr detector. The FT-Raman spectrum of the compound was also recorded over the range of $3000\text{--}1000 \text{ cm}^{-1}$.

The thermal decomposition of β -carotene was carried out in a differential scanning calorimeter DSC (Mettler Toledo). Before measurements, the apparatus was calibrated on the basis of the following standards: the temperature scale on the basis of n-octane and indium and the heat exchange according to the fusion heat of indium, 28.45 J/mg . The process conditions were measurement temperatures ranging from $150\text{--}500 \text{ }^\circ\text{C}$, $20 \text{ cm}^3 \text{ min}^{-1}$ nitrogen flow rate, and $10 \text{ }^\circ\text{C min}^{-1}$ heating rate.

The colour of the obtained composites was measured using a CM-3600d spectrophotometer (Konica Minolta). The radiation source consisted of four impulse xenon tubes. The spectral range of the apparatus was $360\text{--}740 \text{ nm}$, and the change in colour $dE \times ab$ was calculated as follows:

$$dE \times ab = \sqrt[3]{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

where ΔL represents the brightness relationship between light and dark, Δa represents the relationship between green and red and Δb represents the relationship between blue and yellow and symbol Δ implies the difference of colors between the samples before and after ageing.

Oxygen induction time (OIT) tests were performed using a Mettler Toledo DSC instrument. Four-milligram samples were heated from room temperature to the test temperature, 220°C , at a rate of 20°C/min under a nitrogen atmosphere. After 5 min at 220°C , the gas was changed from nitrogen to air at a flow rate of 60 ml/min . When all antioxidants were consumed, the sample began to oxidise, producing a deviation in the baseline. The OIT was measured as the time between the gas switch and an intersection with a tangent from the maximum derivate after oxidation had started. Two analyses of each sample were performed to ensure accuracy in the results.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviour of β -carotene at Pt electrode

The electrochemical oxidation of β -carotene was investigated at a platinum electrode using CV and DPV methods. Representative voltammograms are presented in Figure 1.

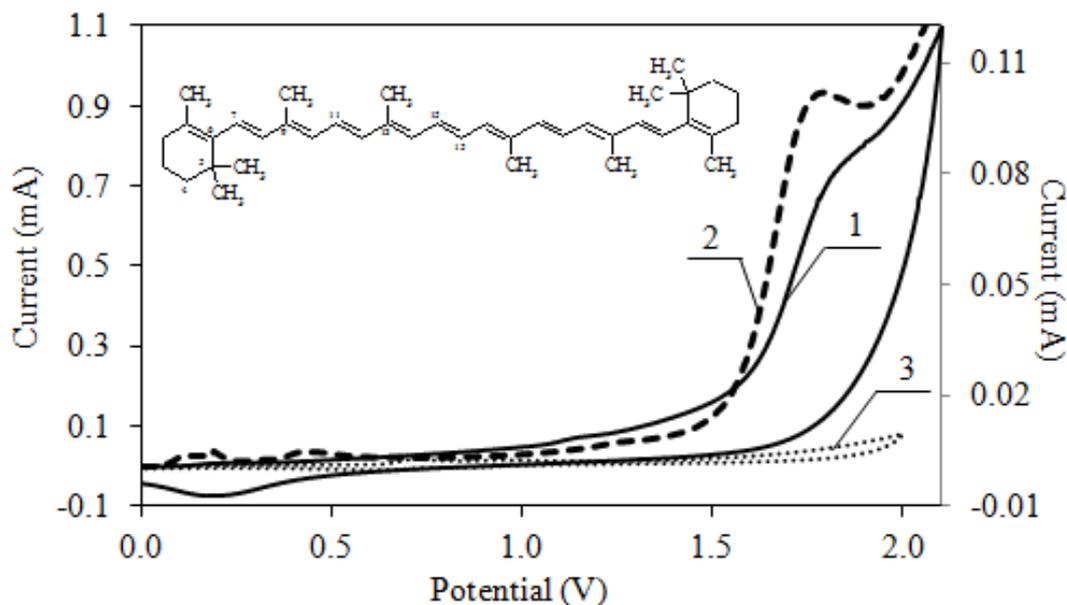


Figure 1. Voltammograms for the electro-oxidation of β -carotene at a Pt electrode; curve 1 - CV, 2 - DPV, 3 - CV recorded in the supporting electrolyte; $c = 5 \times 10^{-4} \text{ mol L}^{-1}$ in $0.1 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NClO}_4$ in acetonitrile, $v = 0.1 \text{ V s}^{-1}$.

The half-wave potential ($E_{1/2}$) determined from the CV voltammogram for the electro-oxidation of β -carotene corresponds to the peak potential (E_p) in the DPV voltammogram. The electro-oxidation of β -carotene was investigated in the potential range in which a supporting electrolyte ($0.1 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NClO}_4$ in acetonitrile) showed no peaks (Fig. 1, curve 3). The voltammograms presented in Fig. 1 (curves 1 and 2) show that β -carotene is most likely irreversibly oxidised in at least one electrode step at potentials lower than the potential at which oxygen evolution starts. The half-wave potential ($E_{1/2}$) for the electro-oxidation of β -carotene determined from the cyclic voltammogram is equal to 1.79 V and corresponds to the peak potential (E_{pa}) determined from the differential pulse voltammogram. Taking into consideration the results of the investigations suggested in papers [34, 35], it can be concluded that the step of the process includes the exchange of two electrons resulting in formation of dication. Irreversibility of this electrode reaction needs to be proved. Moreover useful information involving electrochemical mechanism generally can be acquired from the relationship between peak current and scan rate.

3.2. Effect of scan rate

The scan rate influences the electro-oxidation process of compounds, as previously reported [29, 30]. The effect of the scan rate on the electro-oxidation of β -carotene was investigated in the range from 0.01 to 1.0 V s^{-1} . Representative cyclic voltammograms recorded at different scan rates are presented in Figure 2. An increase in the scan rate resulted in an increase in the peak current determined for the electro-oxidation of β -carotene. In the case of polarisation rates higher than 0.1 V s^{-1} , a new electro-oxidation peak for β -carotene appeared at a potential of 1.15 V. In the reverse scan, a cathodic peak appeared at higher scan rates. Its current also increased as the scan rate increased. This result demonstrates a reduction of products formed during the electro-oxidation of β -carotene. These voltammograms were used in the determination of the anodic peak potential (E_p) and anodic current (i_p).

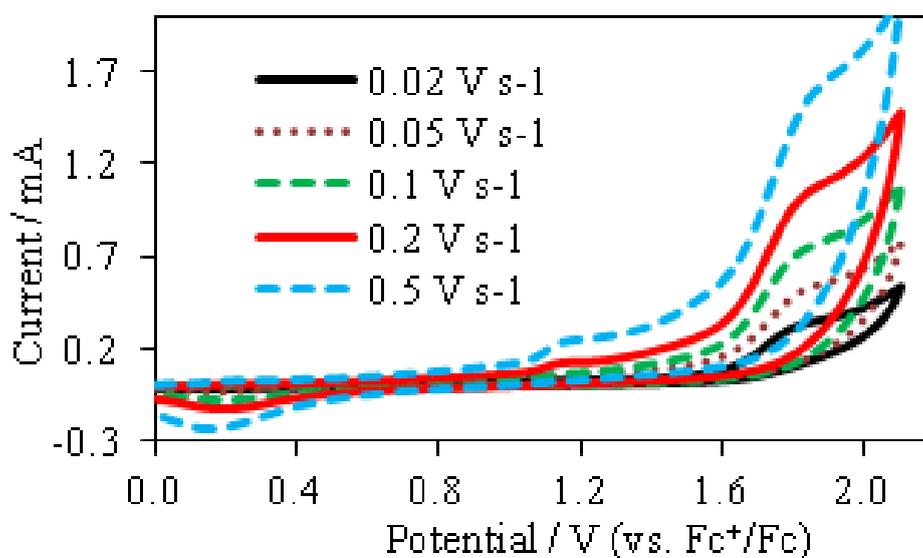


Figure 2. Cyclic voltammograms for the electro-oxidation of β -carotene recorded at a Pt electrode at different scan rates; $c = 5.0 \times 10^{-4} \text{ mol L}^{-1}$ in $0.1 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NClO}_4$ in acetonitrile.

To characterise the electrode reaction for the electro-oxidation of β -carotene, two relationships were determined: i_p vs. the square root of the scan rate ($v^{1/2}$) and the logarithm of i_p vs. the logarithm of the scan rate ($\ln v$). These relationships allow one to determine whether the electrode reaction is controlled by adsorption or diffusion of the substrate to the electrode surface. Fig. 3 shows the dependences determined for the first step of β -carotene electro-oxidation in $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ in acetonitrile. If an electrode reaction is controlled by diffusion, the dependence of i_p vs. $v^{1/2}$ is linear and intercepts the origin. If this dependence does not cross the origin, the electrode reaction can be controlled by adsorption [36-39].

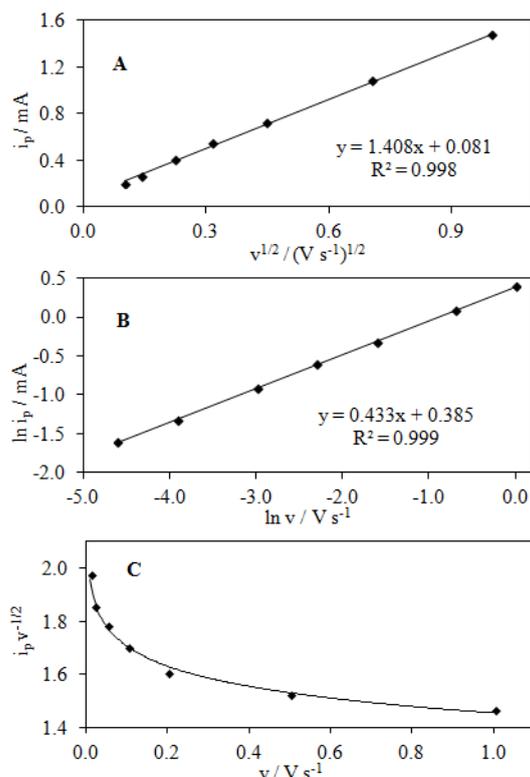


Figure 3. (A) Dependence of anodic (i_{pa}) peak current on the square root of the potential scan rate (v). (B) Dependence of i_{pa} on v in double logarithm coordinates for the oxidation of β -carotene. (C) Variation of the scan rate normalised current ($i_p/v^{1/2}$) with scan rate; $5.0 \times 10^{-4} \text{ mol L}^{-1}$ in $0.1 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NClO}_4$ in acetonitrile at Pt electrode.

In the scan rate range from 0.01 to 1.0 V s^{-1} , the anodic peak current for the electro-oxidation of β -carotene linearly depends on the square root of the scan rate (Fig. 3A) and is described by the following equation:

$$i_{pa} = \{1.408[v(\text{V s}^{-1})]^{1/2}\} \text{mA} + 0.081 \text{ mA}, \quad R^2 = 0.998 \quad (2)$$

The dependence described by equation (1) does not intercept the origin, which may indicate that the electrode reaction is adsorption controlled [40]. However, the linear dependence of $\ln i_p$ vs. $\ln v$, which is presented in Fig. 3B and described by equation (2):

$$\ln i_{pa} = \{0.433 \ln v(\text{V s}^{-1})\} \text{mA} + 0.385 \text{ mA}, \quad R^2 = 0.999 \quad (3)$$

does not confirm such a conclusion.

The slope of this linear dependence is equal to 0.433 and indicates that the β -carotene electro-oxidation reaction is diffusion controlled. Further analysis of the electrode reaction included determining the $i_p/v^{1/2}$ vs. v dependence for the electro-oxidation of β -carotene. This dependence is presented in Fig. 3C. It is clear that the scan rate-normalised current ($i_p/v^{1/2}$) function depends on v . If the process is reversible or irreversible without a preceding or following chemical reaction, the dependence on v should not be observed [40]. The shape of this dependence (Fig. 3C) is typical for an EC mechanism [41-43].

The effect of the scan rate on the potential for the electro-oxidation of β -carotene was also investigated. Figure 4A presents the dependences of peak potential (E_p) vs. the scan rate (v) for the electro-oxidation of β -carotene. These dependences show that the anodic potential becomes more positive if the scan rate increases. This result confirms the irreversible nature of the process.

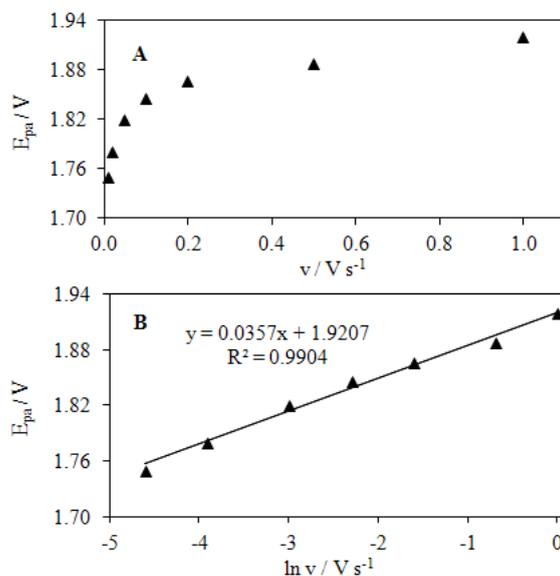


Figure 4. (A) Dependence of anodic (E_{pa}) peak potential on the scan rate (v) for the oxidation of β -carotene. (B) Dependence of E_{pa} on $\ln v$; $c = 5.0 \times 10^{-4} \text{ mol L}^{-1}$ in $0.1 \text{ mol L}^{-1} (\text{C}_4\text{H}_9)_4\text{NClO}_4$ in acetonitrile at Pt electrode.

Moreover, the value of the electron transfer coefficient for the β -carotene electro-oxidation reaction was calculated according to the following equation [38, 44-46]:

$$E_p = \left(\frac{RT}{2\beta n_\beta F} \right) \ln v + \text{const} \quad (4)$$

where E_p - peak potential (V), R - universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), F - Faraday constant ($96,487 \text{ C mol}^{-1}$), T - Kelvin temperature (298 K), βn_β - anodic transfer coefficient, and v - scan rate (V s^{-1}).

This equation can be used in the case of a completely irreversible diffusion-controlled process. The dependence of the anodic peak potential on the logarithm of the potential scan rate is linear and is described by the following equation (Fig. 4B):

$$E_{pa} = \{0.036[\ln v(\text{V s}^{-1})]\} \text{V} + 1.921 \text{ V} \quad R^2 = 0.99 \quad (5)$$

Using the dependence of the anodic peak potential on the logarithm of the potential scan rate (Fig. 4B), the value of the overall electron transfer coefficient (βn_β) for the β -carotene electro-oxidation reaction is equal to 0.36. Cyclic voltammograms recorded for different substrate concentrations were used in the determination of the peak potential (E_{pa}), half-peak potential ($E_{pa/2}$) and half-wave potential ($E_{1/2}$). Based on the determined values, the anodic transfer coefficient (βn_β) and heterogeneous rate constant (k_{bh}) were calculated using previously reported equations [38, 47]. The anodic transfer

coefficient for the β -carotene electro-oxidation reaction is equal to 0.36 ± 0.05 . The heterogeneous rate constant determined at the half-wave potential is equal to $(3.52 \pm 0.05) \times 10^{-4} \text{ cm s}^{-1}$.

3.3. Oxidation processes of β -carotene

The distribution of electron charges in a molecule, which determines the reactivity of the positions of a molecule, is not uniform for the compound examined [33, 48]. The molecular orbital energy (E_{HOMO}) was calculated using the AM1 method as implemented in the HyperChem software. The calculated energy of the highest filled orbital (E_{HOMO} – ionisation potential) determines the ease of electron release and indicates the sites most susceptible to oxidation (Figure 5). The E_{HOMO} for β -carotene is -7.615 eV .

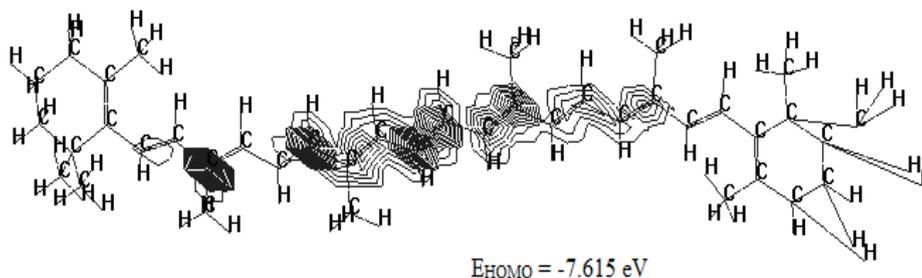
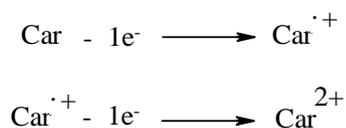


Figure 5. Electron density and probable sites in a β -carotene molecule susceptible to electrooxidation.

The combination of cyclic voltammetry, quantum chemical calculations and the literature data [33, 35] for the oxidation of β -carotene show that the following equations apply (Scheme 1):



Scheme 1. Mechanism for the electro-oxidation of β -carotene, where Car is β -carotene, $\text{Car}^{\cdot+}$ is the radical cation, and Car^{2+} is a dication.

3.4. DSC and FTIR spectroscopy of β -carotene

The melting temperature range was one of the most important parameters for β -carotene (Figure 6).

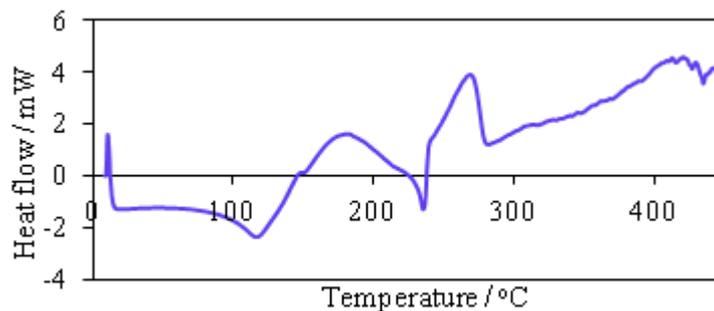


Figure 6. DSC curve of β -carotene.

The melting temperature range of β -carotene were measured by a differential scanning calorimeter (DSC) with the dynamic measurement method. The DSC trace of β -carotene, shows two peaks: the endothermic peak at 174 °C due to the melting process (T_m) and the second peak at 270 °C, an exothermal peak, corresponds to the initial decomposition process for the β -carotene molecule.

FTIR spectroscopy was used to evaluate and analyse this type of compound [49, 50]. The Figure 7 shows the spectrum of β -carotene.

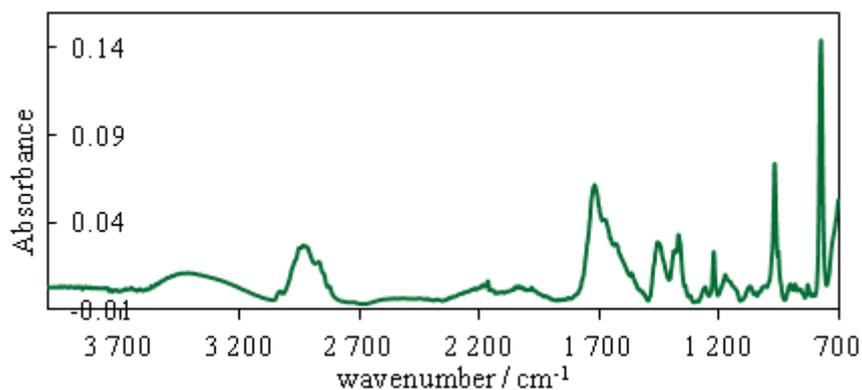


Figure 7. FTIR spectrum of β -carotene.

The β -carotene spectrum exhibited peaks at 2922 cm⁻¹ and 2862 cm⁻¹ for asymmetric and symmetric stretching vibrations of -CH₂ and -CH₃, at 1445 cm⁻¹ for -CH₂ scissoring, at 1360 cm⁻¹ for splitting due to dimethyl group, at 1033 cm⁻¹ for in-plane -CH- and at 962 cm⁻¹ for the trans-conjugated alkene -CH=CH- out-of-plane deformation mode. The absorption changes at 980-930 cm⁻¹ as indicated by the trans =CH stretching band.

3.5. Controlled degradation of Topas composite containing β -carotene

The investigated compound was used to prepare polymeric materials for packaging applications. β -carotene was used to serve as a coloured indicator of ageing time, and as an anti-ageing and antibacterial substance in the polymers. In the first part of the investigation, the effect of β -carotene on the oxidation induction time (OIT) of the Topas composite was assessed. The determined

OIT value indicates that the addition of β -carotene to Topas prolonged the OIT by 2.07 min., which indicates that β -carotene has a protecting effect against the thermo-oxidation of the Topas composite (Figure 8A). The oxidation energy of the composite decreased by 165 J/g compared to that of the reference sample of Topas (Figure 8B).

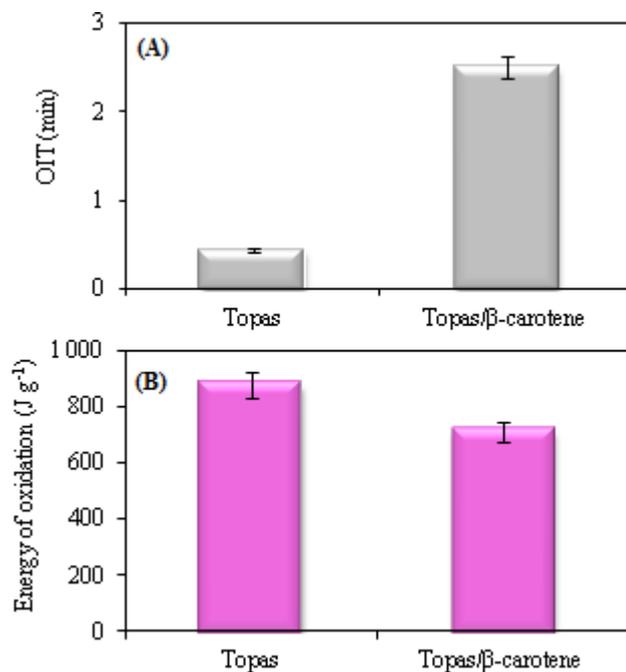


Figure 8. (A) Oxygen induction time (OIT) of Topas composites; (B) Energy of oxidation for Topas composites.

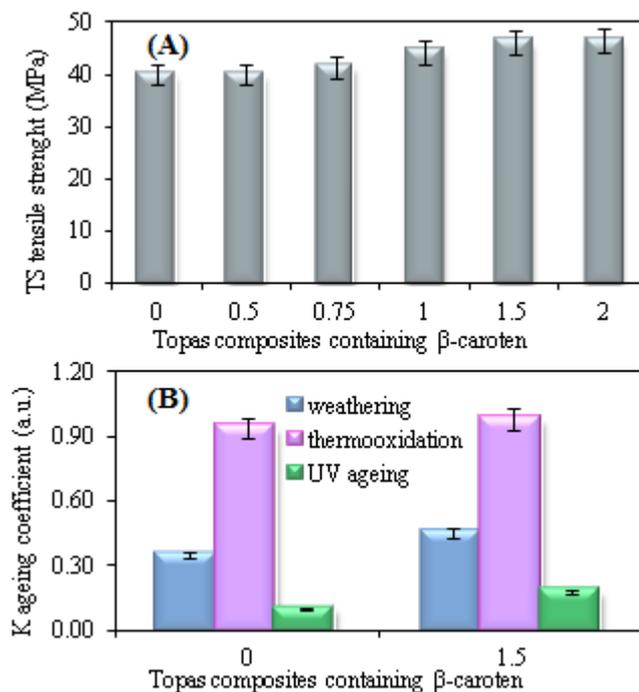


Figure 9. (A) Mechanical properties of Topas composites containing β -carotene; (B) Ageing parameters of the composites subjected to UV, thermal and weathering ageing. K - ageing parameter.

The addition of β -carotene did not change the properties of the Topas thermoplastic composite (Figure 9A), but tests of simulated climatic, UV and thermo-oxidative ageing of Topas composites allowed us to assess the degradation of Topas composites under the influence of various climatic conditions.

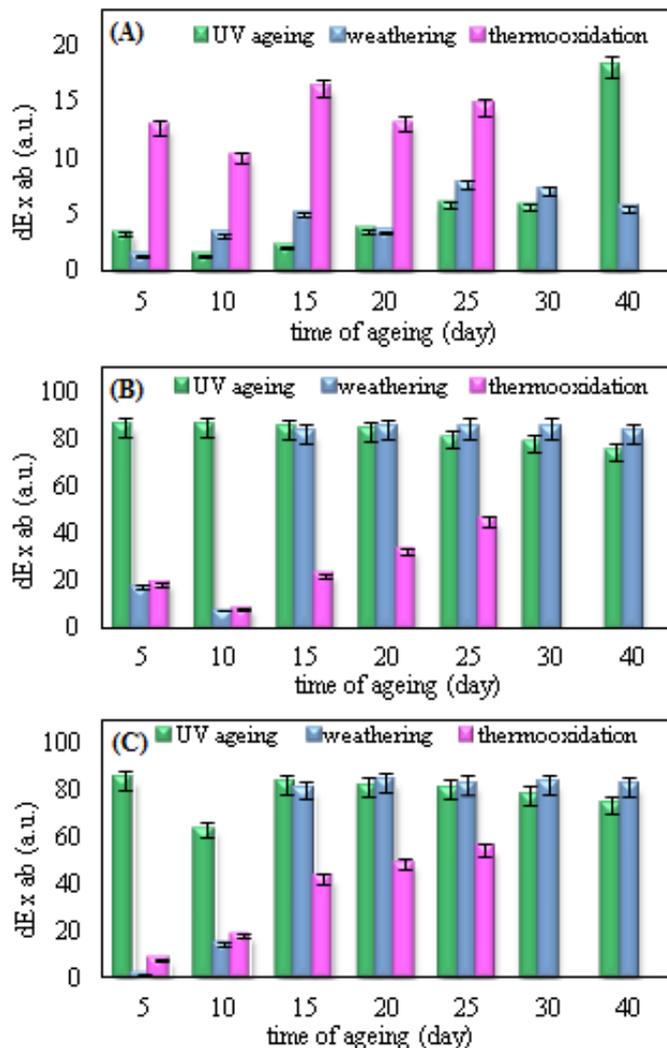


Figure 10. (A) Colour change due to aging (according to CIE-Lab system) of Topas composites; (B) Colour change due to aging (according to CIE-Lab system) of Topas composites containing β -carotene (0.5 phr); (C) Colour change due to aging (according to CIE-Lab system) of Topas composites containing β -carotene (0.75 phr).

Based on changes in the energy of deformation, the parameters of ageing that describe the susceptibility of the material to ageing were determined. According to the determined K values, the composite containing β -carotene has an improved resistance to the action of UV radiation and the synergised climatic conditions compared to that of reference Topas sample (Figure 9B). On the other hand, the addition of β -carotene to the Topas composite resulted in great colour changes in this material under the action of climatic conditions. We measured the colour changes of the Topas material as a function of the ageing time [51-51]. The determined coefficients dE x ab show the extent

of colour change compared to an untreated reference sample. The measurements were conducted for Topas composites that contained various concentration of β -carotene. The colour change of the material was stable up to approximately 10 h under the action of each of the climatic conditions used (Figure 10).

Afterwards, a violent change in the colour of the sample occurred. On the other hand, when the concentration of β -carotene in the material was increased to greater than 1 phr, the colour stability was higher (over 15 h) up to the first considerable change in the value of $dE \times ab$. It appears that β -carotene can serve the role as a working life indicator for the material (Figure 11).

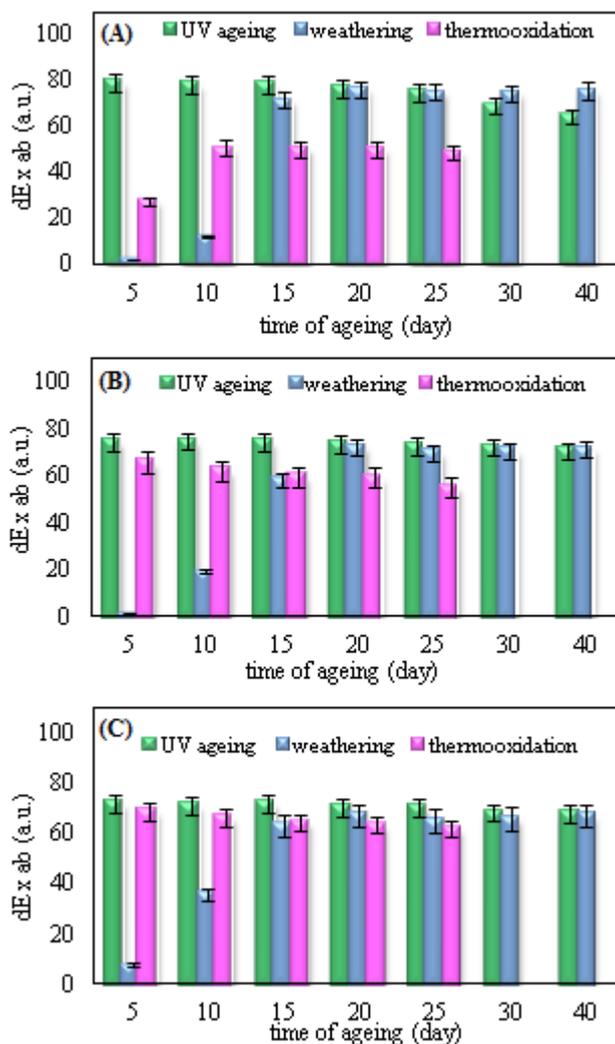


Figure 11. Colour change due to aging (according to CIE-Lab system) of Topas composites containing β -carotene; (A) - 1 phr, (B) - 1.5 phr, (C) - 2 phr.

The colour of β -carotene is exceptionally intense, and the colour changes of the material under the influence of ageing are visible with a naked eye. Therefore, the addition of such a compound to polymers can allow one to impart pro-ecological features to polymeric materials, making them human and environmentally friendly and indicating their working life.

4. CONCLUSIONS

β -carotene is one of the most important food additives because of its various health-related properties. However, its application in the food industry is, at least partially, limited due to its very low water solubility and thermal stability.

The electrochemical behaviour of β -carotene at a Pt electrode in non-aqueous solutions proceeds irreversibly in at least one electrode step before the potential reaches the value at which oxygen evolution starts. The half-wave potential for the electro-oxidation of β -carotene was determined from cyclic voltammograms and was equal to 1.79 V. This value corresponds to the peak potential determined from the differential pulse voltammogram. The β -carotene electro-oxidation reaction is diffusion controlled. The calculated parameters for the electro-oxidation of β -carotene are as follows: the anodic charge transfer coefficient is 0.36 ± 0.05 , and the heterogeneous rate constant is $(3.52 \pm 0.05) \times 10^{-4} \text{ cm s}^{-1}$ (determined at $E_{1/2}$). The β -carotene electro-oxidation process includes the exchange of two electrons in the first step. This step is followed by the chemical reaction. Thus, the investigated process proceeds according to the EC mechanism. Electrochemical measurements and quantum chemistry calculations for the energy of the highest occupied molecular orbital suggest a mechanism for the electrochemical oxidation of β -carotene.

Cyclic and differential pulse voltammetry, FTIR spectroscopy, and thermogravimetric analysis are faster and less expensive methods for analysis than chromatographic methods, which often require large amounts of toxic solvents and long times for analysis. The voltammetric methods are environmentally friendly and can be successfully used to study the antioxidative activity of compounds. The incorporation of β -carotene into the Topas composite improved the stability of materials composed of ethylene-norbornene copolymer. Additionally, β -carotene considerably changed the colour of the Topas composites, serving the role as an indicator for the polymer ageing time as a function of climatic conditions, including UV radiation. The addition of β -carotene to polymeric materials can facilitate the assessment of their working life based on colour changes.

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