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Physico-mechanical analysis of free ethyl cellulose films comprised with novel plasticizers of vitamin resources

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Abstract

This research was conducted to investigate the physico-mechanical characteristics of the EC-based coating membranes plasticized with two informal ingredients of vitamin resources, cholecalciferol and α-tocopherol, with respect to the commercial plasticizer DBS. Proceeding the experiment, free thin polymer sheetings of the sample formulations, incorporating incremental weight percents of the individual plasticizers were prepared employing a revised casting method of delayed solvent evaporation whereby similar flat specimens of standard dimensions were subjected to tensile loadings and extensions. The data were analyzed through the known equations of membrane theory in spherical subjects considering the complete symmetry of assumingly spherical pellets and/or granules. The relative tensile parameters of the experimental and commercial plasticizers in the resilient region were also estimated to fairly decide on a moderate explanation of a strong, hard, and tough structure among the specimens. The results implied the great compatibility of the oily soluble vitamins in EC networks projecting higher factors of safety and greater ultimate strength, toughness, and young coefficient of the formulations compared to the specimens plasticized with the commercial DBS within a concentration range of 40–50% (w/w) of the polymer solids. α-Tocopherol represented supremacy over colecalciferol to result in relatively a 2-fold (and practically a 4-fold with respect to DBS) greater increase in the modulus of resilience. The vitamin compounds and in essential α-tocopherol, in consequence, can properly be applied at concentrations of 40–50% (w/w) as efficient plasticizers to provide a greater protection of the structure against sudden fractures of dynamic and continuously increasing environmental and biological stresses.

Keywords: Ethyl cellulose; Vitamin D_3; Vitamin E; Free film; Plasticizer; Membrane theory

1. Introduction

Ethyl cellulose (EC) is reportedly one of the most widely used high molecular weight compounds, the properties of which have recently been reviewed (Rekhi and Jambhekar, 1995). The cellulose ether appears as a substantially water-insoluble polymer, excessively introduced in the coating structure of solid dosage forms to provide a controlled management on the release profile of drug substances (Lippold et al., 1990; Harris and Ghebre-Sellassie, 1997; Leong et al., 2002). Nevertheless, the polymer is also capable of being incorporated into the majority of other drug delivery systems, such as matrices (Crowley et al., 2004), microspheres (Eldridge et al., 1990), and microcapsules (Jalsenjak et al., 1997), or in combination with other cellulose derivatives (Frohoff-Hülsmann et al., 1999a,b; Duarte et al., 2006) and Eudragits (Lecomte et al., 2004a,b; Siepmann et al., 2005).

EC although primarily applied in organic solutions, is now available as 30% colloidal pseudolatexes. The pseudolatex includes discrete spherical particles of 0.1–0.3 μm in diameter, dispersed in an external aqueous phase (Wheatley and Steuernagel, 1997). Once the EC pseudolatexes are cast or sprayed onto the surface of the desired dosage forms, the dispersion is exposed to gradual water evaporation and polymer deformation. The capillarity forces caused by the high interfacial surface tension of the water droplets entrapped among the polymer chains provide the required driving force to fuse the deformable particles. Similarly, with the organic polymer

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solutions, the bulk of solvent is initially evaporated to continuously increase the viscosity which leaves the polymer chains in close proximity. Upon more complete evaporation of the aqueous phase or the organic solvent, the polymer chains are aligned so that secondary valence forces, either through hydrogen bonds or Van der Waals', are produced between the adjacent chains to further coalesce the polymer into a homogeneous, transparent film (Wheatley and Steuernagel, 1997).

The intermolecular cohesive bonds and in particular the polar and hydrogen bindings among the bulky glucose subunits of ethyl cellulose chains (Bodmeier and Paeratakul, 1994), result in, however, a structure of rigid nature with extremely low deformation and flowability. These structures prevent the effective coalescence of the polymer network during the coating procedure (Bodmeier and Paeratakul, 1991) and thus when exposed to analytical or biological fluids, create an initial barrier against the diffusion which considerably restrict the permeability. The induced osmotic pressure in the internal core region of the coated dosage forms (Ozturk et al., 1990) where after renders the polymer to (micro)rupturing (Nesbitt, 1994) and new-born cracks propagating over the entire entanglement. These cracks would, therefore, be responsible for unexpected drug release and dose dumping phenomenon in delayed release delivery systems.

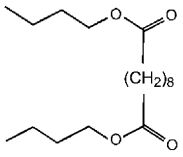
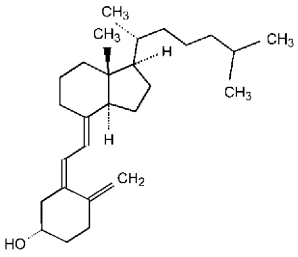
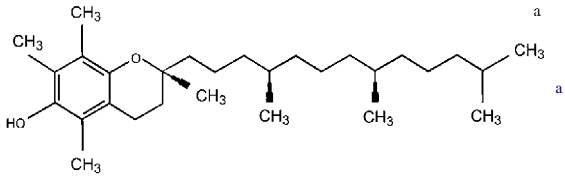
Additionally, when the structure is confronted to high temperatures, most of the bonds can overcome the potential energy barrier against rotation and the segmental or micro-Brownian motion and rotational freedom are increased to result in the chain flexibility and free conformational changes (Sinko, 2006). Thus, at the temperature range, defining as glass-transition or T_g value, the structure is transferred to a rubbery state which can promote the coalescence of the polymer network onto the surface of solid dosage forms. The coating temperature is, therefore, settled on 10–20 °C above the glass-transition temperature by virtue of its potential effect to acquire the activation energies required to break down the secondary valence bonds (Lippold et al., 1989). However, when the temperature is again lowered to the values below the glass-transition, the micro-Brownian motion ceases altogether and the chain conformations are frozen in to retrieve the intermolecular cohesive forces of the rigid and brittle structure.

Following the previous approach, a second way to conquer the rotational barrier is to interpose an intermediate molecule between the adjacent chains to obstruct a great number of the active centers available for the polymer rigid contacts. These molecules increase the free spaces between the chains and provide a higher rotational freedom of the polymer network (Gutiérrez-Rocca and McGinity, 1994; Hyppölä et al., 1996). A reduction in the volume fraction of the intermolecular cohesive bonds result in, subsequently, a decreased T_g value below the coating temperatures, which provide a superior coalescence of the colloidal particles in the pseudolatex or the polymer in the organic solutions (Lippold et al., 1990; Fetscher and Schmidt, 1999). These intermediate compounds, recalled as plasticizers, can potentially reduce the resiliency of the polymer and increase the plasticity of the network when the plasticized structure undergoes the stress loadings during tension or compression.

In general, pliable films of EC are usually constructed by incorporating some plasticizers of long chain esters, such as dimethyl, diethyl, and dibutyl phthalates, triethyl and tributyl citrates, dibutyl sebacate, triacetin and also butyl and glycol esters of fatty acids (Wade and Weller, 1994). Moreover, solid grades of polyethylene glycol have been approved to be compatible enough to form continuous, durable EC membranes and PEG 400 employed at low concentrations of about 5% (w/w) of the dry polymer mass has been proved to result in decisive impact on EC film coatings (Fekete et al., 2006). Among the most widely used plasticizers, such as citrate and phthalate derivatives, no significant differences were observed in the mechanical properties of plasticized EC pseudolatexes films. In addition, the mechanical parameters obtained in the puncture experiments of both dry and wet films, revealed that the commercial EC pseudolatexes (Aquacoat® and Surelease®) and EC organic solutions result in extremely rigid and brittle structures, with rather low puncture strengths and elongation values of lower than 3% at plasticizer concentrations of 20–30% (w/w) (based on the polymer mass) (Bodmeier and Paeratakul, 1994). The recognized low flexibility of the conventional structures may considerably impair the prerequisite stress resistance of the coating which is a distinct disadvantage in applications where coatings of high flexibility and toughness are required (e.g., in tablets compressed from coated beads or cores with deep logos and break lines). Moreover, trivial increases in osmotic pressure induced in the internal region may also provoke the (micro)rupturing and unpredictable release profile of a model drug in dissolution experiments. In a recent analysis (Tarvainen et al., 2003), however, two *n*-alkenyl succinic anhydrides (*n*-ASAs); 2-octenyl succinic anhydride (OSA) and 2-dodecen-1-yl succinic anhydride (DSA), were investigated for their potential to improve the mechanical properties of the discerned rigid EC films. According to the data reported in the tensile loading of the rectangular film samples, plasticized with the two succinic anhydrides, OSA proved to be capable of producing coatings of high elongation and toughness whereas the tensile strengths are not greatly reduced when compared to the commercial plasticizers such as TEC and DBS. As a further indication for a high compatibility limit of OSA with ethyl cellulose, increased film flexibility with concentrations up to 70% (w/w) of OSA (referred to the polymer mass) was observed without any impairment in the resultant values of the film toughness.

In the current study, however, and in continuance to the analysis performed by Tarvainen et al., two new hydrophobic molecules, selected from the natural sources of vitamin groups, have closely been examined for their potential plasticizing effect on EC polymeric films. The choice of the uncommon plasticizers has been resolved upon the concept of the imparted function of cholesterol molecules among the phospholipidal construction of an intact cell membrane. Cholesterol molecules positioned and transferring in between the continuous lipid moiety devotes the required fluidity to maintain a flexible structure, without which the aggregation of the pure lipid components produces a considerably rigid and cement-like structure with little or no biological function (Pollard and Earnshaw, 2002). In consequence, these spacers may be simulated of some immanent

Table 1
Some essential physicochemical properties of DBS and the experimental plasticizers, vitamin D_3 and E

	Dibutyl sebacate	Cholecalciferol	DL-α-Tocopheryl acetate
Molecular formula	$C_{18}H_{34}O_4$	$C_{27}H_{44}O$	$C_{31}H_{52}O_3$
Chemical structure			 [a]
Molecular weight	314.47	384.64	472.74
Boiling point (°C)	344–345[b]	–	184 at 0.01 atm. pressure[b] 194 at 0.025 atm. pressure[b] 224 at 0.3 atm. pressure[b]
Specific gravity	0.934–0.945[c]	0.939[d]	0.952–0.966[e]
Water solubility	Insoluble[f]	Practically insoluble[f]	Practically insoluble

[a] The chemical structure represents for *R*,*R*,*R*-α-tocopherol, the most abundant compound with the greatest bioactivity among the 6-chromanols derivatives of the sub-series tocopherols.
[b] Merck index, 14th ed.
[c] Product information, Fluka Chemie GmbH, USA.
[d] Experimentally determined.
[e] Product information, ATA Roche/Switzerland.
[f] One part of the solute dissolves in over 10,000 parts of water.

plasticizers existing naturally within the mosaic model of the cell membranes. Cholecalciferol, although characterized as vitamin nutrients, has a common precursor originating from the same ancestor with cholesterol (Berg et al., 2007). This molecule may, therefore, resemble some plasticizing potentials attributed to the cholesterol function in vital systems, when incorporated in compositions of similar partitioning effect. Vitamin E recognized as a relevant substituent in the same nutritional category, has also been examined for the probable plasticizing effect in polymeric films. α-Tocopherol is naturally the most abundant and effective chain-breaking antioxidant in the body (Packer, 1991) whose major role in vivo is to stabilize the active free radicals resulting from the oxidation of polyunsaturated fatty acids in cell membranes (Kamal-Eldin and Appelqvist, 1996). The oxidation cascade has also been defined in the lipophilic structure of polyethylene and was hindered in irradiated ultra-high molecular weight polyethylene (UHMWPE), the material of choice for load-bearing articular components in total joint arthroplasty, by diffusion of α-tocopherol to cross-linked polymer (Costa et al., 1998; Oral et al., 2006a,b,c; Reno and Cannas, 2006; Wolf et al., 2006). Moreover, α-tocopherol stabilization did not significantly affect the crystallinity of UHMWPE and was speculated to partly be co-crystallized with UHMWPE to get incorporated into the crystalline lamellae or primarily be placed at the crystal/amorphous interface which may increase the mobility of the chains resulting in a plasticization effect and more efficient quenching of some of the free radicals (Oral et al., 2006a,b,c). The mechanical properties and pin-on-disc wear of α-tocopherol-containing highly cross-linked UHMWPE were not changed when accelerated aged (Oral et al., 2004, 2006a,b,c) which may corroborate to the idea of specific plasticizer–polymer interactions due to the semi-planar structure of vitamin E (Table 1). Vitamins D and E have also been recently reported to strongly be adhered to plastic materials, such as the plastic container of TPN mixtures or namely, the "Big Bags" (Gillis et al., 1983; Allwood, 1984) which may provide a further confirmation to the compatibility of experimental plasticizers with the lipophile-like polymer ethyl cellulose. To define the plasticizing capacity of the two pre-mentioned molecules, the mechanical strength of ethyl cellulose free films containing incremental weight percents of the separate plasticizers were assessed in tension and the resulting data were compared to the corresponding parameters measured for a commercial alternate, DBS. The aim of this study is, therefore, to detect plasticizers of preferentially natural origins (compared to *n*-ASAs) which could imply superior mechanical behavior with smaller amounts contributed in the system, comparing to the common plasticizers applied in commercial products.

2. Materials and methods

2.1. Materials and instrumentation

The ethyl cellulose was provided by Dow Chemical Company, USA (ethoxy content, 48.8% DS; viscosity, 100 mPs). The dibutyl sebacate was obtained from Fluka Chemie GmbH licensed by Sigma–Aldrich Chemie GmbH (USA; product no. 84840; lot and filling code 447503/1, 21904034), and the vitamin compounds D_3 and E were originally produced by ATA Roche/Switzerland as a 1-MIU vitamin D_3 oily solution (batch

no. UT04050022) and DL-α-tocopheryl acetate oily liquid (batch no. UT04080235), respectively. The chemical structure and some physicochemical properties of the commercial and experimental plasticizers are comparatively demonstrated in Table 1. The organic solvent chloroform employed in the present assay was originated of an analytical grade and was exerted as pure and not in combination with other organic liquids to prepare the sequential polymer solutions.

The tensile properties of the polymeric films were examined by the universal testing machine of the series Z100 produced by Zwick/Roell Group, Germany, and employing a 2.0 kN force transducer (load cell) and a pair of 0.5 kN pincer grips. The data were correspondingly analyzed applying the test software testXpert V8.1 (Copyright © 1995–2000, Zwick GmbH & Co.). The machine was equipped with no external strain gauges or namely extensometers and the crosshead travel monitoring or the strain measurements were typically managed based on the entire gauge length of the specimens.

2.2. Free film preparation

To prepare the free films of ethyl cellulose, casting has been selected as the most fundamental method employed in numerous literatures and the total procedure was outlined according to the general specifications of a tensile experiment. In summary, a balanced surface is first adjusted by precisely leveling a plane table in space, applying a proper bubble tube (Clarke, 1983) followed by subsequent trials to manually modify the possible plane deviations and improve the balancing accuracy. The leveled surface is, substantially, an essential key to prohibit the non-uniform thickness distribution along the film, growing mainly due to the unequal spreading of the polymer solution in different regions of the cast. The nominal dimensions of the specimens were also standardized according to both ASTM D882 and ISO 527-1, being equal to 10 and 150 mm for the width and the length of a rectangular flat sample, with 2.5 cm left on both endings to retain a gauge length of 100 mm at the beginning of the test, respectively. In compliance with the desired shape and dimensions of the specimens and to further promote the accuracy of the test, an individual cast with an internal area of 15 cm × 30 cm and 2.5 cm depth was prepared out of (float) glass to provide about 30 similar 1-cm width specimens among which 10–12 of the least producing variations were selected as the final results. The nominal gravity centers for both the cast and the plane surface were determined and the dry clean cast was then placed onto the plane by their centers coinciding to each other. The sample EC solutions were prepared by dissolving 3.1 g of the polymer in about 100 ml of the solvent chloroform and adding the experimental amounts of the three plasticizers with respect to the total dry polymer mass and in accordance to the weight percent increments in Table 2. The average densities of DBS was reported to be 0.936 (0.934–0.945) mg/ml by the manufacturer and the mean densities of cholecalciferol and α-tocopherol oily liquids were experimentally evaluated to about 0.939 and 0.9601 mg/ml, respectively. The mixture was stirred for an hour and left for a further 8–10 h to better homogenize the solution; just prior to use, the solution was again shaken for a few minutes and relaxed for a while to remove the air bubbles. The mixture was then poured into the cast from a distance above the central point and the cast was immediately covered by a piece of nylon cloth wrapped around the walls to fix the sheath. This resulted in a remarked reduction of the solvent evaporation which proved to develop a considerably smooth appearance of the upper surface of the film with respect to the time the solvent is freely vaporizing.[2] The cast was left motionless for about 18–20 h where upon it was semi-filled with cold water after the solvent was completely dried out. The collateral sides of the rectangular film were precisely separated by means of a surgical blade (code no. 11-1*a*) and then left for the water to gradually rise up the separated film from the underlying cast plane. The sheeting was dried on a blotting paper and reserved at room temperature and relative humidity (23 ± 2 °C and 50 ± 5% RH) for about 72 h prior to test. Just before the experiment, the length of the polymeric films were divided into 25–30 1-cm width strips and the mass and dimensions of the individual specimens were recorded to 0.1 mg and 1/2 mm precision, respectively. An extra piece of 2.0 cm × 0.5 cm was also cut out of each film, the dimensions and the mass were similarly recorded and its average thickness was visually measured under a light microscope and a 40× objective magnification. The average area and density was then calculated for the sample according which a theoretical means was obtained to estimate the mean thickness of each strip in a series of specimens.

Table 2
Plasticizer concentrations in EC test solutions

% (w/w)	Plasticizers		
	DBS	Vitamin D_3	Vitamin E
0	P	P	P[a]
10	+	+	+
20	+	+	+
30	+	+	+
40	+	+	+
50	+	+	+
55	−	−	+[b]
60	+	+	+
70	+	+	+
80	−	−	+

[a] Pure ethyl cellulose films.
[b] Confirming formulation in the test series.

The tests were managed with an extension speed and acceleration of 0.5 mm/s and 0.5 mm/s^2, respectively, and the nominal stress–strain diagrams together with the registered parameters for a usual tensile experiment (Geres and Timoshenko, 1990b) were recorded as σ_s (the stress values in N/mm^2 or MPa) for σ_y (the yield stress or the stress at the yield point), σ_{max} (the maximum tensile strength), σ_B (the stress at break), and ε_s (the strains or the percent elongations) for ε_y (the yield strain), and ε_B

[2] This effect which is probably due to the improved coalescence of the polymer network during elongated evaporation is particularly comparable to the thermal influence of the post-treatment affair and may result in, however, reduced stress-concentrating centers (Geres and Timoshenko, 1990a) within the polymer, providing a more uniform physical response under extension.

(the strain at break). The young-modulus or the modulus of elasticity, E (in N/mm^2 or MPa), and the toughness modulus or the energy at break, U_B (in MJ/m^3), were, respectively, recognized in the resilient region based on a tangent model and through the integration of the stress–strain curve from the beginning to the fracture.

2.3. Mechanical experiments—theory of membranes and shells

Assuming that a pharmaceutical core pellet resembles a doubly curved closed pressurized vessel shown in Fig. 1, when the mean thickness of the coating layer h, coalesced onto the surface of the pellet, is supposed to be small as compared with the radii of curvature of the shell surface r_θ and r_φ (i.e., $h < 0.1 r_\theta$ and r_φ), the ratio of bending stresses to membrane stresses is regarded as negligible leading to the state of stress at any point within the coating structure be satisfactorily explained according to the issue of membrane theory. The precision of the equations and results are, however, confirmed inasmuch as the shell is freely expandable in all directions (Timoshenko and Woinowsky-krieged, 1959; Budynas, 1999).

Isolating an element of the coating membrane using coordinates tangent to the principal arcs of curvature and perpendicular to the surface, the dimensions of the element would, therefore, be equal to $r_\varphi \Delta\varphi$ by $r_\theta \Delta\theta$ by h, and the outward normal of the infinitesimal surface is established by n. The state of stress on the element is shown in Fig. 1a, where for the equilibrium of forces in the n direction projects

$$-2\sigma_\theta h r_\varphi \Delta\varphi \sin\frac{\Delta\theta}{2} - 2\sigma_\varphi h r_\theta \Delta\theta \sin\frac{\Delta\varphi}{2} + p r_\theta \Delta\theta r_\varphi \Delta\varphi = 0 \tag{1}$$

Since $\Delta\theta$ and $\Delta\varphi$ are infinitesimal, $\sin(\Delta\theta/2) = \Delta\theta/2$ and $\sin(\Delta\varphi/2) = \Delta\varphi/2$ which by simplifying the previous equation obtains

$$\frac{\sigma_\theta}{r_\theta} + \frac{\sigma_\varphi}{r_\varphi} = \frac{p}{h} \tag{2}$$

The stress in the radial direction σ_r is assumed to be zero toward the outer surface of the vessel and p at the inner surface. The pre-assumed loadings are also considered to be of tensile type, due to an increased flexibility of the shell under compressive forces exerted in the same direction as tension. The general shape and geometry of the membrane, regarding the profoundly small thickness of the sheeting, is virtually responsible to confront with great bending moments and shears to render the shell to numerous folding along the length. It is also assumed that the structure is submitted to distribute loadings on all over the surface to prevent the undefined influence of the increased stresses produced by the concentrated loadings in tension. To reduce a second relationship for the membrane stresses σ_θ and σ_φ, a symmetric break is usually made in the vessel so that only one of the stresses exists along the break, and the stress is determined using the equilibrium condition of the isolated element.

Taking the considerations of a complete spherical shape of the core pellet and the coating structure of the radius r, a perfect

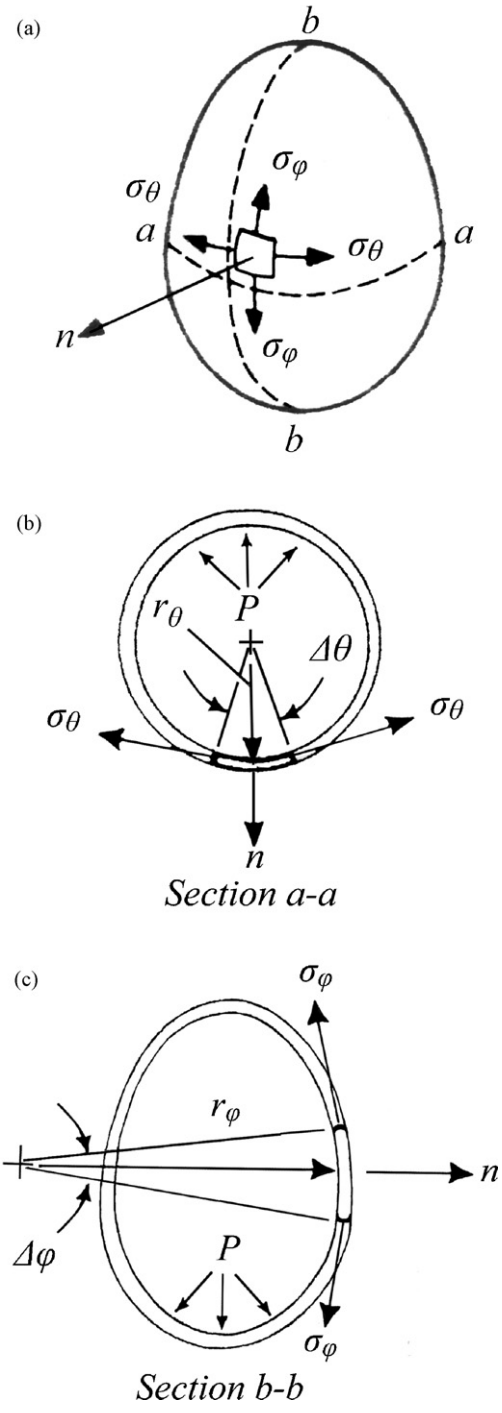


Fig. 1. Thin-walled pressure vessel.

symmetry of the system is provided resulting in $r_\theta = r_\varphi = r$. The stress components σ_θ and σ_φ are, therefore, equal to each other and Eq. (2) yields

$$\sigma_\theta = \sigma_\varphi = \frac{pr}{2h} \tag{3}$$

where the value p in a pharmaceutical system of pellet dosing, immersed in analytical or biological fluids, is assumed to hold for the absolute resultant of forces acting upon the external and internal surfaces of the shell in the n direction. Supposing that

the radius r, the coating thickness h, and the medium influence p on the shell structure are similar for all formulations, definite quantities are obtained for either of the terms involved in Eq. (3), reducing equal membrane stresses acting on the shell. Considering the stress value σ or its respective components σ_θ and σ_φ approach their maximum probable quantities in natural biological fluids, $\sigma_{\max}^{(\text{bio.})}$, the actual strength of the coating should therefore be greater than the maximum stress by a factor of n (i.e., the factor of safety) to preclude the premature failure of the shell (Geres and Timoshenko, 1990c) where upon the fault may remark on a defected release profile in dissolution experiments. The factor of safety for each specimen is theoretically derived with respect to a determinate $\sigma_{\max}^{(\text{bio.})}$ and the mean ultimate or yield strength of the sample obtained during tensile experiments.

$$\text{Factor of safety} = \frac{\text{Mean actual strength}}{\text{Maximum biological stress}}$$

$$n_i = \frac{\sigma_i}{\sigma_{\max}^{(\text{bio.})}} \tag{4}$$

In actual practice, however, it is more important for the majority of compounds to remain fairly within the linearly elastic region to exclude permanent strain configurations of the structure due to great plastic deformations beyond the yield point. The polymer entanglements, likewise, produce an initial stiffness due to the resiliency of the polymer which supports the expected functions of the system especially in release studies. Once the structure is exposed to aqueous media, although is pressurized by the surrounding environment, if the loadings are assumed not to be greater than the yielding stress the polymer is expected to efficiently recover its initial shape and resistance after the loads are removed. The polymer would therefore retrieve its original porosity network by which the permeant diffuses through the coating layer resulting in rather unchanged release properties during dissolution experiments. When the loadings are continuously increased or by sudden dynamic loadings implied on the shell structure, the polymer would finally yield where after by further increase in the force exertion, the entanglement is rendered to large plastic deformations and structural changes re-orientating the chains to induce some alterations in the functional capacities of the polymer membrane. The porosity network and the apparent tortuousity is, therefore, rearranged which may further result in an increase or reduction of the diffusivity and permeability of the polymer in regard to diminished porosity or to the contrary the increased tortuousity of the structure. So that, it seems most suitable for the polymer constructions to implement the yield strength of the compound to proceed the safety factors of the various formulations. The expression (4) is, therefore, transformed into:

$$n = \frac{\sigma_{\text{y}}}{\sigma_{\max}^{(\text{bio.})}} \tag{5}$$

which for two separate formulations yields

$$n_i = \frac{\sigma_{\text{y}}^{i}}{\sigma_{\max}^{(\text{bio.})}}$$

and

$$n_{i+1} = \frac{\sigma_{\text{y}}^{i+1}}{\sigma_{\max}^{(\text{bio.})}}$$

Comparing the two factors of safety, n_i and n_{i+1}, produces the parameter α which returns the yield strength ratio for two membranes made, by convention, of the same concentration of two different plasticizers or systems of plasticizers,

$$\alpha = \frac{n_{i+1}}{n_i} = \frac{\sigma_{\text{y}}^{i+1}/\sigma_{\max}^{(\text{bio.})}}{\sigma_{\text{y}}^{i}/\sigma_{\max}^{(\text{bio.})}}$$

or

$$\alpha = \frac{\sigma_{\text{y}}^{i+1}}{\sigma_{\text{y}}^{i}} \tag{6}$$

The linear relationship between stress and strain of a prismatic bar in simple tension has been expressed by the Hooke's law (Geres and Timoshenko, 1990d);

$$\sigma = E\varepsilon$$

in which E denotes for the modulus of elasticity from the zero strain to the yield point.

Substituting the respective values of σ from the Hooke's equation in the ratio α (Eq. (6)), results in

$$\alpha = \left(\frac{E_{i+1}}{E_i}\right)\left(\frac{\varepsilon_{i+1}}{\varepsilon_i}\right) = \beta \cdot \kappa$$

or

$$\beta = \frac{\alpha}{\kappa} \tag{7}$$

where $\beta = E_{i+1}/E_i$ and $\kappa = \varepsilon_{i+1}/\varepsilon_i$. Thus, a second parameter β, denotes for the stiffness ratio of two structures plasticized with the same weight percent of different materials and when expressed in correlation with α values represents the comparative elastic toughness of two formulations based upon the theories of strain energy (Higdon et al., 1985; Geres and Timoshenko, 1990e). Considering the concept of strain energy as $\int \sigma \, \mathrm{d}\varepsilon$, it represents the area under the stress–strain curve and when evaluated from zero to the elastic limit (for practical purposes, the proportional limit), yields a property known as the modulus of resilience defined as the maximum strain energy per unit volume that a material will absorb without inelastic deformation. Thus,

$$u = \int_{\varepsilon_i}^{\varepsilon_n} \sigma \, \mathrm{d}\varepsilon = \frac{1}{E}\int_{\sigma_i}^{\sigma_n} \sigma \, \mathrm{d}\sigma = \frac{1}{2E}(\sigma_n^2 - \sigma_i^2)$$

and

$$u_{\text{y}} = \int_{0}^{\varepsilon_{\text{y}}} \sigma \, \mathrm{d}\varepsilon = \frac{1}{2E}(\sigma_{\text{y}}^2 - 0)$$

or

$$u_{\text{y}} = \frac{\sigma_{\text{y}}^2}{2E} \tag{8}$$

in which u_{y} is the modulus of resilience or the elastic strain energy intensity expressed for a particular yield strength. Eval-

uating the modulus of resilience for two structures containing equal weight percents of different plasticizers, therefore, provides,

$$u_{\mathrm{y}}^{i} = \mathrm{AUC}]_{\mathrm{yield}}^{i} = \frac{(\sigma_{\mathrm{y}}^{i})^2}{2E_i}$$

and

$$u_{\mathrm{y}}^{i+1} = \mathrm{AUC}]_{\mathrm{yield}}^{i+1} = \frac{(\sigma_{\mathrm{y}}^{i+1})^2}{2E_{i+1}}$$

Accordingly, comparing the two elastic strain energies per unit volume of the membranes yields

$$\gamma = \frac{u_{\mathrm{y}}^{i+1}}{u_{\mathrm{y}}^{i}} = \left(\frac{\sigma_{\mathrm{y}}^{i+1}}{\sigma_{\mathrm{y}}^{i}}\right)^2 \cdot \left(\frac{E_i}{E_{i+1}}\right)$$

or

$$\gamma = \frac{\alpha^2}{\beta} \tag{9}$$

where γ indicates the relative elastic toughness modulus for two different plasticizing systems among the various formulations.

In the current study, the three parameters α, β, and γ are separately evaluated for formulations of different plasticizers or systems of plasticizers in regard to the formulation with corresponding percent of the commercial plasticizer DBS. In other words, the index i of the variables denotes for the respective values of stress, elastic modulus, and the toughness moduli of the polymer membranes plasticized with the same concentration of the commercial DBS.

3. Results and discussions

3.1. The influence of DBS on mechanical representations of EC membranes

The mean values of the mechanical properties together with the standard deviations of 10–12 repetitions of each formulation are obtained for DBS-plasticized specimens in Table 3. The maximum strength and the strength at break of the polymer construction has been revealed to be the same in tensile experiments and therefore, the maximum strength $\sigma_{\max}$, has been substituted the ultimate strength in the tables.

In addition, to further clarify the mechanical response of the coating formulations with the plasticizer percent, the variation rate of the individual parameters with incremental concentrations of the plasticizer are found by taking the regression of the parameter values against the concentration (Table 4). As it is obvious from the Table, the respective values of the stress, strain, and the young coefficient may follow up either a linear or exponential profile to continuously increase (the strain at break) or gradually decrease (the ultimate strength and the young-modulus) by sequential addition of the plasticizer into the polymer solutions. In other words, with higher amounts of the plasticizer introduced into the organic mixture, greater numbers of DBS molecules take the possibility of contribution to the extended polymer, intervening the contact polymer–polymer

Table 3
Tensile values of EC films plasticized with incremental concentrations of DBS

DBS (%, w/w)	Thickness (μm, S.D.)	Mass (mg, S.D.)	*E*-modulus (MPa, S.D.)	$\sigma_{\max}$ (MPa, S.D.)	ε_{B} (%, S.D.)	σ_{y} (MPa, S.D.)	ε_{y} (%, S.D.)	U_{B} (MJ/m^3, S.D.)
0	58.0 (7.7)	88.5 (11.7)	864.26 (53.82)	38.35 (1.46)	6.83 (0.41)	38.41 (1.50)	6.83 (0.41)	1.18 (0.18)
10	56.0 (4.8)	89.0 (7.6)	770.55 (58.74)	27.84 (1.69)	7.13 (0.78)	27.81 (1.70)	6.90 (0.61)	1.04 (0.21)
20	74.2 (9.9)	104.7 (11.3)	472.20 (20.02)	16.17 (0.50)	11.48 (1.20)	14.23 (0.58)	5.91 (0.34)	1.27 (0.19)
30	72.2 (4.5)	109.4 (6.9)	374.59 (12.29)	13.05 (0.40)	25.74 (2.72)	9.88 (0.39)	5.59 (0.60)	2.53 (0.33)
40	88.9 (3.2)	127.4 (4.6)	241.71 (12.77)	9.84 (0.36)	43.59 (3.79)	7.18 (0.18)	6.27 (0.67)	3.31 (0.31)
50	81.5 (5.0)	122.9 (7.5)	113.64 (8.07)	4.27 (0.14)	45.17 (4.86)	4.13 (0.14)	8.70 (0.85)	1.69 (0.21)
60	99.3 (12.5)	133.7 (12.9)	41.59 (4.35)	2.47 (0.17)	50.29 (4.66)	2.31 (0.17)	11.29 (0.95)	1.09 (0.11)
70	122.3 (7.6)	167.9 (10.4)	25.48 (2.40)	2.11 (0.05)	55.35 (4.72)	1.87 (0.04)	15.17 (0.87)	1.02 (0.08)

Table 4
Bimodal regressions of tensile parameters in DBS- and vitamin-plasticized EC films

Plasticizer system	σ_{max} (MPa)	σ_y (MPa)	ε_B (%)	*E*-modulus (MPa)
DBS	$y = -0.5754x + 33.26$; $R^2 = 0.9205$[a]	–	$y = 0.8028x + 2.5992$; $R^2 = 0.9379$	$y = -11.991x + 771.02$; $R^2 = 0.9225$
	$y = 42.967\,e^{-0.0446x}$; $R^2 = 0.9692$	$y = 39.032\,e^{-0.0448x}$; $R^2 = 0.9924$	$y = 6.8617\,e^{0.0346x}$; $R^2 = 0.8988$	$y = 1296.1\,e^{-0.0524x}$; $R^2 = 0.9474$
Vitamin D_3	$y = -0.3922x + 28.62$; $R^2 = 0.9105$[b]	–	$y = 1.6188x - 3.7444$; $R^2 = 0.9727$	$y = -9.5854x + 752.59$; $R^2 = 0.9367$
	$y = 35.109\,e^{-0.0128x}$; $R^2 = 0.9665$	$y = 35.109\,e^{-0.0128x}$; $R^2 = 0.9665$	$y = 8.5994\,e^{0.0388x}$; $R^2 = 0.9071$	$y = 959.62\,e^{-0.0307x}$; $R^2 = 0.969$
Vitamin E	Variable	Variable	Variable	Variable

[a] The regression has been concluded in the range of 0–60% (w/w) DBS concentration.
[b] The regression is concluded in the region of 0–70% (w/w) vitamin D3 in the solution.

forces of the adjacent chains. The entrapped molecules in EC entanglement nullify a great volume of the inter-chain cohesive forces through the new polymer–plasticizer bindings which result in a significant decline in the yield or ultimate strength and hardness of the constructed membranes. The local mobility is similarly increased in accordance to a reduction in the attractive forces of the polymer network which retains the increased percent of elongation and ease of deformation under a much lower mechanical loading. The respective values of the toughness modulus or the strain energy stored in the system are, however, attributed to the variations in both the stress and the strain of the compound and by virtue of the fact the stress is decreasing and the strain increasing, the AUC which is an integrative value of the both conjugates, first increases up to a maximum and is then continuously reduced to very low values. The increased toughness modulus, in general, provides a higher protection of the structure against the impact of the dynamic loadings (Geres and Timoshenko, 1990f) and therefore the maximum area under the stress–strain diagram is generally desired among the various formulations plasticized with incremental concentrations of different plasticizers.

Referring to Table 3 for subsequent values of the stress and strain, the strain is conceived to be negligible in the beginning, representing a brittle structure at plasticizer concentration less than 30%, while the polymer is rendered to considerably great deformations in the extreme mentioned limit of the plasticizer content, indicating a perfectly plastic nature of the formulation. The stress, in comparison, projects great values at plasticizer concentrations below 30% while it is continuously diminished to reduce considerably weak structures at plasticizer percents more than 50% (w/w) of the polymer solids. At a moderate concentration of 40% (w/w) of the plasticizer DBS, both the stress and the strain acquires intermediate quantities upon which the integrative energy represents a maximum in its corresponding series of specimens. The confirming vision of this phenomenon is established in the cumulative diagram of the average curves produced from the several repetitions of a specified formulation as illustrated in Fig. 2. As it is also obvious in the compiling diagram, the EC membranes plasticized with the commercial DBS produce a rather stiff and strong structure of brittle nature at plasticizer concentrations of less than 30% whilst in concentrations more than 50% (w/w) (i.e., the three end formulations) a profoundly soft and weak plastic construction is produced.

3.2. The mechanical influence of vitamin D_3 as an informal plasticizer in EC membranes

To assess the mechanical behavior of the membranes plasticized with incremental concentrations of vitamin D_3, the average tensile parameters and standard deviations of the test specimens in the series profile are obtained in Table 5. The bimodal regression of the parameters variation with respect to incremental weight percents of the plasticizer in the polymer solution are correspondingly expressed in Table 4. Deducing from the tables, linearity is still persisting among the corresponding values of the ultimate strength, strain at break, and the young-modulus through both a zero- and first-order profile. Just the same as the case with the commercial DBS, the yield strength variation projects a merely exponential regression to mildly decrease with incremental weight percents of the plasticizer, vitamin D_3. The stress (both the ultimate and the yield strength) and the *E*-modulus progressively decrease in value while the strain percent increases with an increase in the plasticizer concentration

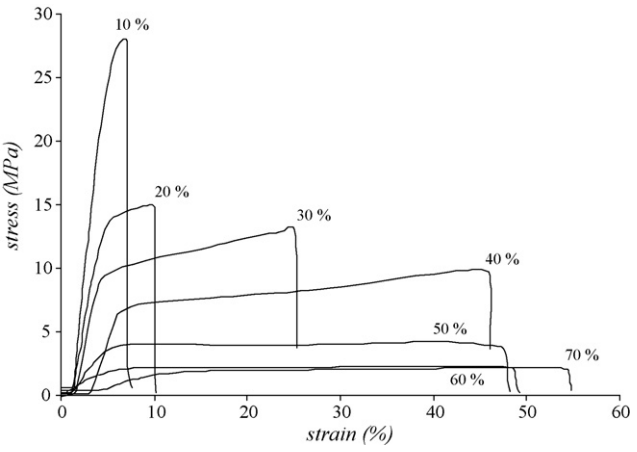


Fig. 2. Average stress–strain diagrams for DBS-containing specimens concerning different plasticizer concentrations in the polymer solution.

Table 5
Tensile parameters of EC films plasticized with incremental concentrations of vitamin D_3

Vitamin D_3 (%, w/w)	Thickness (μm, S.D.)	Mass (mg, S.D.)	*E*-modulus (MPa, S.D.)	σ_{max} (MPa, S.D.)	ε_B (%, S.D.)	σ_y (MPa, S.D.)	ε_y (%, S.D.)	U_B (MJ/m^3, S.D.)
0	58.0 (7.7)	88.5 (11.7)	864.26 (53.82)	38.35 (1.46)	6.83 (0.41)	38.41 (1.50)	6.83 (0.41)	1.18 (0.18)
10	73.6 (12.0)	99.7 (16.3)	663.39 (34.89)	29.09 (0.77)	7.67 (0.40)	29.02 (0.86)	7.67 (0.40)	1.08 (0.14)
20	76.5 (8.9)	111.2 (13.0)	509.98 (54.98)	25.13 (2.30)	23.45 (1.77)	19.08 (1.43)	6.60 (0.35)	4.34 (0.63)
30	87.5 (7.9)	118.3 (10.7)	412.69 (30.18)	23.54 (1.42)	38.67 (3.57)	14.11 (0.38)	6.50 (0.15)	6.33 (0.82)
40	78.0 (3.0)	121.1 (4.7)	343.39 (14.87)	22.16 (1.19)	53.45 (4.47)	11.89 (0.37)	6.78 (0.22)	7.80 (0.86)
50	96.6 (8.1)	130.7 (13.1)	214.84 (13.76)	20.08 (0.72)	82.93 (2.43)	7.66 (0.24)	7.96 (0.54)	9.58 (0.55)
60	104.1 (5.6)	147.0 (7.5)	111.10 (8.48)	15.06 (0.86)	104.35 (4.32)	4.45 (0.18)	8.40 (0.74)	8.15 (0.55)
70	105.1 (11.2)	140.1 (15.0)	120.24 (4.09)	14.28 (0.56)	111.28 (3.69)	4.32 (0.12)	8.24 (0.46)	7.99 (0.39)
80	114.9 (8.2)	153.8 (11.0)	82.72 (5.68)	12.95 (0.75)	120.42 (3.68)	3.43 (0.09)	8.84 (0.62)	7.55 (0.50)

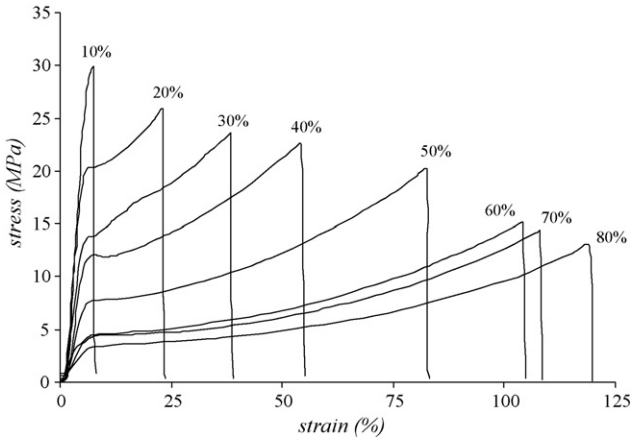


Fig. 3. Average stress–strain diagrams for vitamin D_3-plasticized specimens regarding incremental weight percents of the vitamin in the polymer solution.

introduced into the system; however, the rate of decrease in the strength and the young-modulus and the slope of increase in the percent of elongation are, respectively, lower and higher in the regressions for vitamin D_3 compared to the values recorded for the plasticizer DBS. The deformation rate of the linear regression in vitamin D_3-containing systems is approximately 2-folds higher than the DBS-including specimens whilst the rate of decrease in the ultimate strength, with respect to linear regression, is simultaneously 2-folds lower for D_3- than the DBS-containing films. The slope of linear reduction in the young-modulus is correspondingly 20–25% lower for the latter plasticizer which with respect to the increased stress and strain results in relatively a three-time increase in the maximum toughness at a concentration of about 50% (w/w) of the vitamin D_3. Further inspection in the cumulative diagram of the average stress–strain curves in Fig. 3 declares that the system does not merely represent a perfectly plastic feature at high concentrations of the plasticizer, but it recommends a strain hardening effect which increases the strength before the sample fracture takes place and the slope of increase of the maximum strength is continuously reduced by further increase in the amount of the plasticizer.

To follow up the course on vitamin D_3, the relative tensile parameters for the respective formulations plasticized with the same percent of either the two compounds are estimated through the expressed parameters α, β, and γ and the values are obtained in Table 6. The correlative diagrams of the factors α, β, and γ against the plasticizer concentrations are correspondingly illustrated in Fig. 4 in which the α values represent a continuously progressive approach in subsequence to an increase in the percent of plasticizer, whereas the β ratios tend to remain rather constant or holding with very slight inclination in the initial values after which a profound increase in the β results in rather a steep rise in the ratio baseline. Interestingly, the γ quantity which is the cumulation of the α and β ratios gradually increases up to a maximum with an imitative slope of the α profile where after represents a great reduction in accordance to the sudden increase of the β measurements. Therefore, the maximum strain energy intensity in the resilient region is produced by an approximate

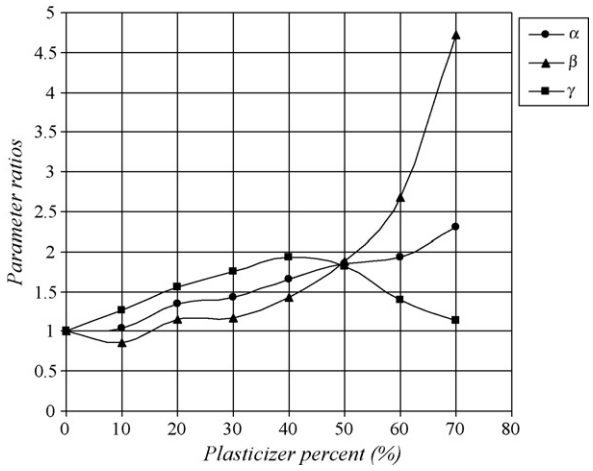


Fig. 4. Cumulative diagram of parameter ratios for vitamin D_3-plasticized membranes.

concentration of the plasticizer, vitamin D_3, within the range of 40–50% (w/w) of the polymer solids which provides a safety coefficient of almost 2 times greater than the commercial DBS to permanent plastic deformation.

3.3. Mechanical observations for vitamin E-plasticized specimens

The mechanical values obtained for a series of incremental vitamin E-containing specimens in Table 7 reveal that the variation rates of the individual parameters do not simply follow up a linearly increasing or decreasing profile but a sensible deviation and a slight deflection is perceived from the usual linear regressions at, respectively, the concentration shifts from 20 to 30% and 60 to 70% (w/w) of the incorporated plasticizer. The stress, in general, represents a sudden reduction of the original value by employing a merely 10% of the plasticizer in the polymer solution, while the strain percent in Table 7 does not seem to remark on any perceptible deformation just similar to the case with the two previous plasticizers; the stored energy at the moment of fracture, therefore, represents a half reduction in the quantity in accordance to the sudden decrease in the tensile strength. However, when the amount of plasticizer is increased

Table 6
Relative tensile parameters for vitamin D_3- and DBS-plasticized specimens

Plasticizer (%, w/w)	Parameter ratios		
	α[a]	β[b]	γ[c]
0	1.000	1.000	1.000
10	1.044	0.861	1.265
20	1.341	1.151	1.562
30	1.428	1.168	1.747
40	1.656	1.421	1.930
50	1.855	1.891	1.820
60	1.926	2.671	1.389
70	2.310	4.719	1.131

[a] Yield strength ratio.
[b] Stiffness ratio.
[c] Elastic toughness modulus ratio.

Table 7
Tensile parameters of EC films plasticized with incremental concentrations of vitamin E

Vitamin E (%, w/w)	Thickness (μm, S.D.)	Mass (mg, S.D.)	*E*-modulus (MPa, S.D.)	σ_{max} (MPa, S.D.)	ε_B (%, S.D.)	σ_y (MPa, S.D.)	ε_y (%, S.D.)	U_B (MJ/m^3, S.D.)
0	58.0 (7.7)	88.5 (11.7)	864.26 (53.82)	38.35 (1.46)	6.83 (0.41)	38.41 (1.50)	6.83 (0.41)	1.18 (0.18)
10	65.2 (6.9)	98.5 (10.5)	782.25 (49.21)	28.84 (2.85)	5.67 (0.44)	28.84 (2.85)	5.67 (0.44)	0.62 (0.13)
20	74.1 (11.8)	109.5 (17.3)	592.07 (30.16)	30.41 (0.78)	9.19 (0.47)	30.41 (0.78)	9.19 (0.47)	1.51 (0.19)
30	88.4 (12.8)	125.0 (18.0)	362.86 (20.87)	31.84 (2.60)	60.73 (5.48)	14.77 (0.72)	8.39 (0.42)	12.33 (0.18)
40	91.0 (10.0)	122.4 (13.4)	314.73 (20.94)	32.94 (2.48)	68.07 (4.05)	13.77 (1.44)	9.94 (0.48)	13.63 (1.34)
50	94.6 (10.0)	133.2 (14.1)	303.98 (20.73)	34.05 (2.15)	79.17 (4.95)	13.26 (0.45)	11.01 (0.68)	15.63 (1.49)
55	97.9 (14.5)	136.1 (20.1)	268.42 (17.92)	31.11 (0.97)	74.68 (5.40)	12.75 (0.76)	11.71 (0.41)	13.88 (1.13)
60	117.2 (11.6)	156.5 (15.5)	146.18 (11.60)	23.50 (1.73)	100.64 (5.62)	6.85 (0.76)	11.50 (0.65)	12.44 (0.93)
70	108.9 (10.7)	151.7 (15.0)	185.47 (14.84)	25.42 (1.04)	93.46 (5.65)	8.48 (0.77)	10.14 (0.83)	13.00 (0.98)
80	111.6 (9.9)	155.0 (13.8)	126.23 (5.82)	20.80 (1.74)	105.57 (6.01)	6.73 (0.10)	12.72 (0.38)	11.99 (1.26)

to 20% of the polymer solids, the maximum strength, in contrast to the previous similar considerations in DBS- or vitamin D_3-including systems, projects a surprisingly further increase in the value which gradually rises up to a maximum at an average concentration of 50% (w/w) vitamin E. The stress thereafter decreases until it reduces a second slight rise at 70% (w/w) of the plasticizer after which the value is again diminished to lower quantities. Once the concentration of the plasticizing molecule is increased from 20 to 30%, the percent of elongations in the respective formulations lead to a sudden 6.6-fold increase in the straining of the samples which with respect to the growing considerations of the strength component and a simultaneous 1.7-fold decline in the young-modulus, appoint for an appreciably 8.2-fold increase in the toughness modulus. The strain energy is progressively increased to apprehend a maximum at 50% (w/w) vitamin E after which the value is reduced to confront the second rise in correspondence to the stress function at 70% of the plasticizer. The existence of a secondary maximum is also confirmed by, respectively, a slight reduction and a trivial increase in the corresponding values of the strain and the *E*-modulus as it is observed from the subsequent records in Table 7.

The double-strength increasing phenomenon is probably due to the intra- and inter-chain disposition of the plasticizing molecule which may reduce the great compactness of the EC entanglement at the first introduction into the system with a plasticizer concentration of 10%. The molecular structure of α-tocopherol as depicted in Table 1 consists of an aromatic cromophore with two functional groups plus a long aliphatic side chain which may expose the semi-planar molecule to easily interpose in spaces where the more bulky structures of DBS and cholecalciferol are not able to introduce. Moreover, it can also be speculated of the two oxygen groups in the planar moiety to intermediate between the two adjacent chains to substitute the polymer–polymer forces with polymer–plasticizer–polymer interactions through the unsubstituted OH– groups in the polymer structure. The aliphatic side chains in α-tocopherol molecules may also provide an additional hydrophobic interaction with the lipophilic ethoxy groups of the ethyl cellulose polymer resulting in further strength of the attractive forces and to firmly cling the plasticizer in position between the chains. The new plasticizer bindings may probably be stronger than the polymer initial cohesive forces by virtue of the fact the strength value of the system is progressively increasing in accordance to an increase in the number of bindings produced at incremental concentrations of the plasticizer. Nevertheless, the inter-chain spaces are steadily increased by a continuous addition of the plasticizing molecules resulting in a progressive reduction in the polymer compactness. In other words, although the plasticizer interference may increase the whole strength of the network, the total straining effect and elongation of the entanglement is improved which further diminishes the maximum strength of the structure; the strength-increasing event is, therefore, not perfect and is not able to approach its initial values or higher. The local chain mobility is correspondingly increased whereby at a 30% concentration of the plasticizer, the polymer conformation is rearranged to hold the possibility

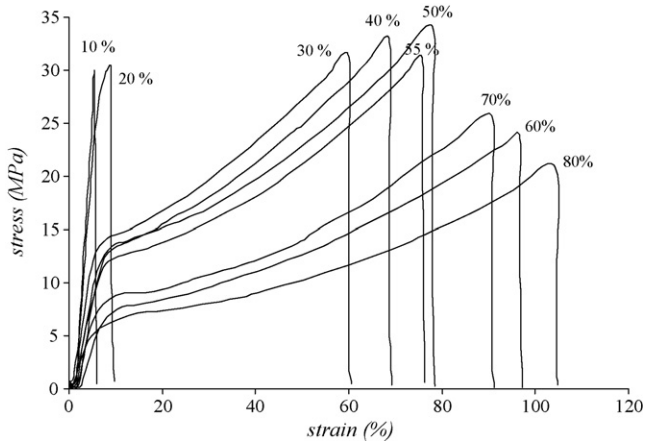


Fig. 5. Average stress–strain diagrams for vitamin E-plasticized membranes including different weight percents of the plasticizer in the polymer solution.

of a sudden increase in the elongating ability of the structure. However, with the concentrations of higher than 50% (w/w), the acquired strength of the polymer is immediately reduced which may be theorized by the increased number of plasticizer molecules intervening in the polymer–plasticizer–polymer forces to produce two separate polymer–plasticizer bonds; the local displacements are, therefore, increased and the strength of the structure is greatly reduced to take a rather similar pathway as the case with the two previous plasticizers. In essential, the above discussion virtually emanates from the nominal stress–strain diagrams and necessarily more information is needed to exactly demonstrate the feature of plasticization with vitamin E. In a further trial, the great impact of the plasticizer on EC membranes is also apparent in the cumulative diagram of the median curves (Fig. 5) which represents a great strain hardening of the polymer immediately after the yield point.

The DBS- and vitamin D_3-plasticized specimens are also strain hardened after the yielding phenomenon, but the amount and the slope of hardening are, respectively, lower with DBS- and D_3-containing films.

Finally, to quantify the analysis, the relative tensile parameters, α, β, and γ and their correlative diagrams are obtained in Table 8 and Fig. 6, respectively, for further comparison.

Table 8
The relative tensile parameters for vitamin E- and DBS-plasticized specimens

Plasticizer (%, w/w)	Parameter ratios		
	α[a]	β[b]	γ[c]
0	1.000	1.000	1.000
10	1.037	1.015	1.059
20	2.137	1.323	3.453
30	1.495	0.969	2.307
40	1.918	1.302	2.825
50	3.211	2.543	4.054
60	2.965	3.515	2.502
70	4.535	7.279	2.825

[a] Yield strength ratio.
[b] Stiffness ratio.
[c] Elastic toughness modulus ratio.

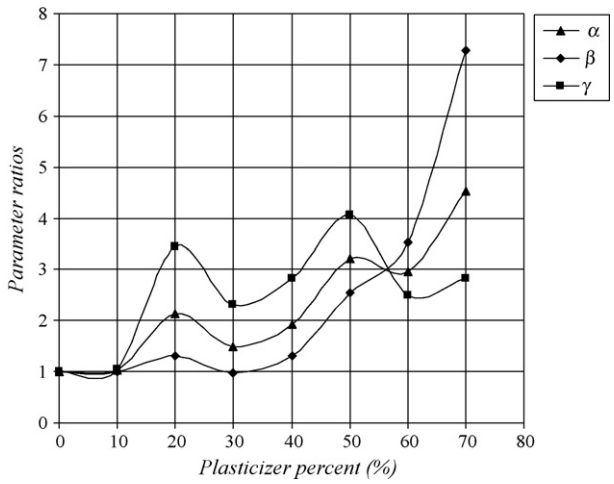


Fig. 6. Cumulative diagram of parameter ratios for vitamin E-plasticized specimens.

As it is obvious in the figure, the yield strength ratio α, develops a non continuous increasing pattern while the stiffness ratio β, slightly increases up to a concentration of 40% of the vitamin where after instantly rises up to factors of 7.3-fold higher values in the ending concentrations. The relative strain energy γ, stored in the specimen is also appeared as a non continuous, step-wise profile with a maximum at 50% of the plasticizer and two lower energy peaks at, respectively, 20% and 70% of the plasticizing substance. In addition, referring to the table of parameter ratios for vitamin D_3 (Table 6), an almost 4-fold increase in the relative toughness modulus is obtained at an approximate concentration of 50% (w/w) vitamin E which with respect to a 2-fold increase in the γ value with vitamin D_3, represents a 200% more efficient plasticizer in supporting the structure against the permanent deformation.

3.4. General comparison of different plasticizers toward the internal resistance of the matter to ultimate fracture and plastic deformations—linear regression versus exponential regression for elastic and ultimate strain energy variations

The elastic toughness modulus, conveying the concept of interior resistance to permanent plastic deformation, is actually correlated to the area under the proportional region of the nominal stress–strain diagram from zero to the yield point (with ε_y and σ_y as, respectively, the abscissa and ordinate) and is best defined as the modulus of resilience (Eq. (8)) or the elastic strain energy intensity of the matter. Generally, in load-displacement experiments, the higher the value of toughness modulus, the greater resistance is obtained against plastic straining and the yield strength or strain occurs in correspondingly greater values in stress–strain diagram. The γ expression (Eq. (9)) which entails relative quantities for the modulus of resilience of two separate formulations, is virtually defined by the simultaneous products of two distinctive ratios ($\sigma_y^{D_3,E}/\sigma_y^{DBS}$) and ($E_{DBS}/E_{D_3,E}$). As depicted in the cumulative diagrams of Figs. 4 and 6, the γ equation in 0–70% (w/w) of either the experimental to commercial plasticizers appears as a markedly smooth and irregular bell-shaped entity proceeding, respectively, the model of vitamin D_3 and E to DBS within which the relative magnitudes accomplish with an average maximum at a moderate concentration of 40–50% (w/w) of the vitamin ingredients. Generally, when the continuous function $f(C)$ in the closed distance [0, C_t] (C denotes as the concentration of the plasticizer involved in the current measurements of the γ statement) develops an absolute extremum in the value C_{max}, the respective quantities of the function recognize an ascending variation in the distance [0, C_{max}] followed by a descending direction in [C_{max}, C_t]. The general slope of function in individual segments proves a positive and negative orientation in, respectively, the pre- and post-maximum values which finally approach to zero at a critical concentration as C_{max}. Similarly, concerning the two relative functions of γ equation, one of the parameter ratios should essentially insist on a continuous increase whilst the other one should rigidly maintain with a general decrease of the respective quantities upon which the multiplication of corresponding values designates an absolute maximum with opposite slopes in either sides of γ_{max}. Alternatively, if both of the relative functions (i.e., the yield strength and the E-modulus ratios) establish a continuous increase or decrease of the inter-series variations, the sequential γ measurements object a thoroughly ascending or descending outline with gradual increments in the plasticizer content.

Referring to different regressions of tensile parameters expressed in Table 4, the σ_y variations is conceived to exclusively correlate with a continuously exponential regression with vitamin D_3-plasticized specimens representing a lower slope of reduction in the yield strength of the matter with respect to DBS-containing films. So that, in consequence to the above discussion and according to the illustration in Fig. 4, the relative factor α which indicates for the yield strength ratio of vitamin D_3- to the same concentration of DBS-containing systems projects a definitely ascending exponential in the limit 0–70% (w/w) of the two plasticizers. The relative function β, in comparison, as demonstrated in Table 4, may correlate with both a linear and exponential regression to configure the inter-series relation; if the current variations of elastic modulus are assumed to be linear with incremental concentrations of DBS- and vitamin D_3-contaning specimens, both the regressions represent a negative coefficient upon which the relative factor β (and also the reciprocal β^{-1}) acquires an oppositely positive slope to progressively increase with additional plasticizer in the solution. Thus, the ascending α and β^{-1} ratios induce a continuously increasing profile for γ interpolation indicating that the modulus of resilience is progressively increased with subsequent amounts of plasticization.

However, when exponential regressions are assumed to implement with β variations, by virtue of the greater influence of DBS in reducing the young coefficient to incremental concentrations of vitamin D_3 in polymer solutions (Table 4), the reciprocal function β^{-1} constitutes a descending exponential with a negative slope upon which the concurrent values of the γ equation project a continuous function in the limit 0–70% (w/w) of the plasticizer with a distinguished extremum at approximately 40–50% (w/w) of vitamin D_3 and DBS.

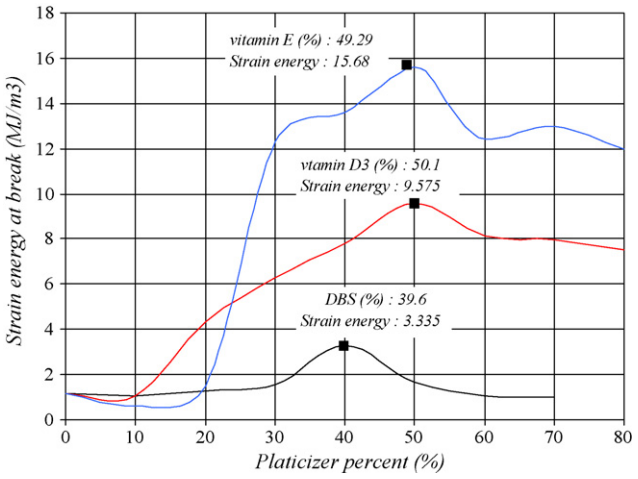


Fig. 7. The comparison of ultimate strain energy in DBS-, vitamin D_3-, or vitamin E-plasticized specimens concerning different weight percents of the plasticizers.

Interestingly, the inter-series variation of other tensile parameters including σ_{max} and ε_B, may also correlate with similar exponential regressions which due to very low magnitudes of negative and positive slopes may erroneously pretend as a linear sketch. Additionally, further inspection in Tables 6 and 8 reveals that the affording γ measurements apprehend a maximum quantity at approximately 50% (w/w) of vitamin E which with respect to the same weight percents of DBS and vitamin D_3 in relative formulations propose a, respectively, 4- and 2-fold greater resistance to plastic deformations. Correspondingly, the ultimate strain energy, U_B, which associates with the internal resistance to fracture, is conveniently defined as the area under the stress–strain diagram from zero to the break (i.e., $\int_0^{\varepsilon_B} \sigma \, d\varepsilon$), and is mutually contributed to the variations of σ_{max} (equal to σ_B in the present assay) and ε_B for a general decision on the maximum toughness among the specimens. As it was pointed out in the previous discussion made for the elastic toughness modulus, the exponential regressions of σ_{max} and ε_B (Table 4) corresponds to a continuous decline and a progressive inclination of the ultimate strength and maximum percent elongation of the sample, respectively, which proclaim a discriminate extremum for the integral function. Moreover, simultaneous comparison of ultimate toughness modulus resolved by the three plasticizers in Fig. 7 reduces that a maximum strain energy is approached at a moderate concentration of about 50% (w/w) of vitamin E which with respect to the maximum quantities in DBS- and vitamin D_3-including systems projects a, respectively, 4.7- and 1.6-fold higher values for the membrane strain energy. Thus, the internal resistance of the coating formulations against fracture represents by a rough estimation, a 500% and 150% greater increase with 50% vitamin E to, respectively, 40% (w/w) DBS and 50% (w/w) vitamin D_3.

4. Conclusion

In subsequence to mechanical analyses performed to assess the plasticizing effect of the oily soluble vitamins in EC networks, the lipophilic α-tocopherol and cholecalciferol molecules remark on a transcendent compatibility with the polymer construction probably due to the semi-planar moiety of the vitamins structure in spatial configurations. The vitamin disposition in EC networks, re-orientates the polymer chains to promote the general compactness resulting in hard and strong structures of great toughness which with respect to particularly the miscellaneous unsymmetrical loadings and/or increased dynamic forces of the true biological environments provide a better protection of the whole structure against sudden fractures and increased elongations. The great plastic deformation of the yielded polymer, although may provide a partial resistance to premature failures of the coating membrane (expressed as dose dumping phenomenon of the defected dosage forms in controlled-release studies) is not capable of completely restoring the original characteristics to accomplish the desired release properties of the effective system. The vitamins interference in EC networks, in comparison to DBS or other commercial plasticizers, increase the actual strength and inherent toughness of the polymer in the resilient region resulting in greater safety coefficients in biological fluids. The vitamin E, in essential, implies a greater influence to vitamin D_3-consisting films on polymer mechanics and with respect to DBS-containing systems provides an approximately 300 and 400% increase in, respectively, the strength and toughness of the polymer to improve the yielding tolerance within a concentration range of about 40–50% (w/w) of the plasticizer.

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