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Development of photoresponsive coumarin-modified ethylene-*co*-vinyl alcohol copolymers with antifouling behavior



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ABSTRACT

Keywords: Ethylene-co-vinyl alcohol copolymers Coumarin Modification Reactive groups Photo-responsive Coating Antifouling In this work, the modification of ethylene-*co*-vinyl alcohol (EVOH) copolymer with a coumarin derivative, 7-(hydroxyethoxy)-4-methyl coumarin (HEOMC), has been performed through the incorporation of different reactive groups, *p*-nitrophenyl chloroformate, succinic anhydride and phthalic anhydride as different linkers between coumarin and EVOH with the aim to obtain photo-responsive materials with improved protein absorption resistance. After purification, the modification degree was calculated by nuclear magnetic resonance and ultraviolet-visible spectroscopy. The thermal properties revealed the crystallinity loss and higher maximum degradation temperatures when EVOH is modified with coumarin derivative. Copolymers were successfully photocrosslinked through the photo-responsive behavior of coumarin moieties. The micro-hardness test shown an increase of the mechanical performance due to the coumarin presence. The water contact angle measurements revealed that while coumarin-modified EVOH copolymers present a higher hydrophilic behavior than EVOH, the photo-dimerization process mainly leads to slightly deviations on the surface wettability of neat EVOH. Finally, the absorption of bovine serum albumin onto the surface of the coumarin-modified materials revealed enhanced antifouling properties, particularly after the photo-crosslinked process. Therefore, the introduction of coumarin through different chain extenders leads to functional materials with tunable photo-responsive performance and protein absorption resistance.

1. Introduction

The development of copolymers is an effective tool for modifying polymeric systems and therefore, to increase the number of applications in the industry. Ethylene-*co*-vinyl alcohol (EVOH) copolymer is a thermoplastic and semicrystalline copolymer synthesized from ethylene and vinyl acetate and posterior hydrolysis. EVOH presents good mechanical and optical properties, it keeps low permeability to O₂ and CO₂, and consequently it is a very suitable material for the development of inner layers in high barrier multilayer films for food packaging [1]. The hydroxyl groups of EVOH provide a high cohesive energy to the system, by leading to a decrease in the available free volume for exchange of gas and high oxygen barrier properties [2], also providing suitable hydroxyl sites to be easy used for further functionalization [3]. The ethylene molar content in EVOH is essential to determine characteristics like the melting point (T_m) or the glass transition temperature (T_g), which are also important for the processability of EVOH [4].

However, the presence of -OH groups triggers the absorption of water and provokes a decrease in the physical and mechanical

properties. For this reason, an optimal method to reduce their affinity against water molecules is the partial modification of –OH groups. Thus, EVOH copolymers can be easily modified to obtain materials with tunable properties [5].

Coumarin is a natural compound habitually used in polymer chemistry due to their photo-responsive properties [6,7]. Coumarin derivatives are able to experiment reversible photo-dimerization and pho-cleavage processes under UV irradiation. At wavelengths close to 365 nm, the double bond near to the lactone group undergoes a $[2\pi + 2\pi]$ cycloaddition to form a cyclobutane ring [8]. The dimers can be photo-cleaved into monomers under irradiation of a UV light ($\lambda < 260$ nm). These photochemical properties are used in the development of different photo-responsive polymeric systems [9,10] like micelles [11], nanogels [12], nanocomposites [13] as well as shape memory polymers [14].

Besides, many coumarin derivatives have the capability to stabilize free radicals, generally leading to good anti-oxidant and anti-microbial activity [15]. These properties have also been used to enhance the thermal stability of several polymers [7,16], or to provide antimicrobial

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behavior [17], respectively. Coumarin can also be effective as antifouling agent due to its lipophilic character and planar molecular structure [18,19]. In opposition to metallic biocides, coumarin is an environmental-friendly system to be incorporated in polymer coatings, affecting the biofilm formation and the progress of fouling sequence, as is the case when coumarin is incorporated into the matrix paints [20].

In this study, commercial EVOH copolymer with 56% of vinyl alcohol content is modified with coumarin to give enhanced and new properties such as photo-responsive behavior and antifouling properties. The EVOH is previously activated following three different strategies by incorporation of *p*-nitrophenyl chloroformate, succinic anhydride or phthalic anhydride. The substitution degree in each case is calculated by nuclear magnetic resonance (¹H NMR) and ultravioletvisible (UV–vis) spectroscopy. The resulting materials with coumarin are characterized by Fourier Transform Infrared Spectroscopy (FTIR), ¹H and ¹³C NMR. The photo-responsive properties are studied to evaluate the photo-dimerization and photo-cleavage of grafted coumarin moieties. In order to use these materials as potential polymer coatings, the thermal behavior, microhardness, surface wettability and antifouling properties are also analyzed.

2. Experimental section

2.1. Materials

with 56% of vinyl alcohol EVOH copolymer (density = 1.15 g cm^{-1} , melt flow index = g 10 min⁻¹) was supplied by 1,4-dioxane, 2,2-dimethoxypropane, N,N'-dicyclohex-Dupont, ylcarbodiimide (DCC), dichloromethane (DCM), ethyl acetoacetate, resorcinol, 2-bromoethanol, ethyl acetate, 4-(dimethylamino)pyridine (DMAP), triethylamine (TEA), potassium carbonate, N,N-dimethylformamide (DMF), phosphorous pentoxide, p-nitrophenyl chloroformate, succinic anhydride, tetrahydrofuran (THF), phthalic anhydride, bovine serum albumin-fluorescein isothiocyanate conjugate (BSA-FITC) and Trizma[®] hydrochloride buffer solution (pH = 7.4) were supplied by Sigma-Aldrich. Acetone, DMF, n-hexane, chloroform, ethanol and methanol, were supplied by Scharlau. Sulfuric acid (98%), dimethyl sulfoxide (DMSO) and pyridine were supplied by Panreac. Nmethyl-2-pyrrolidone (NMP) and deuterated DMSO were supplied by Merck. TEA was distillated before used; the other products were used as received.

2.2. Synthesis of coumarin derivative

The synthesis of the coumarin derivative was carried out by following the procedure of Ling et al. [21] with some variations. Equimolar amounts of resorcinol (35.6 g, 0.32 mol) and ethyl acetoacetate (42.15 g, 0.32 mol) were dissolved in 130 mL of 1,4-dioxane. Then, 9.7 mL of concentrated sulfuric acid (182 mmol) were added dropwise and stirred for 3 h at 65 °C. The reaction was cooled down to room temperature and the white precipitate was filtered and washed with hexane to obtain pure 7-hydroxy-4-methylcoumarin (HMC). Later, HMC (4 g, 22.7 mmol) was poured in a two-neck round-bottom flask and dissolved in 20 mL of DMF. Then, 2-bromoethanol (4.3 g, 34.4 mmol and potassium carbonate (6.3 g, 45.6 mmol) was added under stirring. The reaction mixture was stirred for 24 h at 88 °C, then cooled down and poured into ice water; the crude product was filtered and recrystallized twice in ethyl acetate to obtain 35.2 g of HEOMC (yield ca. 50%).

¹H NMR (400 MHz, CDCl₃, ppm): 7.51 (d, 1H; J = 8.8 Hz), 6.88 (dd, 1H; J1 = 8.8 Hz, J2 = 2.8 Hz), 6.83 (d, 1H, J = 2.8 Hz), 6.15 (d, 1H, J = 1.2 Hz), 4.15 (t, 2H, J = 4.4 Hz), 4.02 (q, 2H, J = 4.9 Hz), 2.40 (d, 3H, J = 1.2 Hz), 2.09 (t, 1H, J = 6.0 Hz, OH). FTIR: ν (cm⁻¹) = 3427, 2954, 1704, 1621, 1554, 1388, 1370, 1295, 1272, 1268, 1153, 1074, 1042, 892, 893, 867, 846, 817, 752, 573, 526, 441.

2.3. Synthesis of HEOMC-succinic acid (HEOMCO)

The synthesis of the coumarin derivative was achieved by following the procedure described in a previous work [13]. In a rounded flask, HEOMC (2.10 g, 9.52 mmol) was dissolved in 25 mL of DCM and TEA (5.32 mL, 38.1 mmol) was added. In another flask, succinic anhydride (1.52 g, 14.26 mmol) and DMAP (57.5 mg, 0.47 mmol) were dissolved in 30 mL of DCM. The solution of HEOMC was poured into the second flask and the mixture was stirred at room temperature for 72 h. The solution was filtered, washed with a 5% HCl solution and purified by recrystallization in ethanol to obtain 2.44 g (yield ca. 80%) of HEOMCO.

¹H NMR (400 MHz, DMSO, ppm): δ 7.70 (d, J = 8.7 Hz, 1H), 7.05–6.96 (m, 2H), 6.23 (d, J = 1.5 Hz, 1H), 4.42–4.27 (m, 4H), 2.41 (d, J = 1.3 Hz, 3H). ¹³C NMR (101 MHz, DMSO, ppm): δ 173.8, 172.6, 161.7, 160.6, 155.1, 153.8, 127.0, 113.8, 112.9, 111.8, 101.9, 67.0, 62.8, 29.1, 18.6. Electron-ionization mass spectroscopy (EI-MS): m/z calculated for C₁₆H₁₆O₇ [M + H]⁺: 320.0896, found: 320.0902. FTIR: ν (cm⁻¹) = 3098, 3025, 2993, 2955, 2931, 1726, 1656, 1606, 1556, 1391, 1369, 1339, 1301, 1208, 1148, 1080, 1029, 983, 905, 875, 851, 833, 795, 747, 705, 667.

2.4. Synthesis of HEOMC-phthalic acid (HEOMC-PH)

In a rounded flask, 5 g of HEOMC (22.70 mmol) and 4.7 mL of TEA (34.05 mmol, 1.5 eq.) were dissolved in 100 mL of anhydrous THF under Argon atmosphere. In another two-necked rounded flask provided with a condenser, 5 g of phthalic anhydride (34.05 mmol, 1.5 eq.) and 138 mg of DMAP (1.13 mmol, 0.05 eq.) were dissolved in 30 mL of anhydrous THF. Afterward, the solution of HEOMC was added with a syringe over the phthalic solution and the mixture was stirred at reflux for 72 h. The mixture was cooled down to room temperature and the salt of TEA was filtered. Then, the solution was concentrated, washed with aqueous 5% HCl and extracted with DCM. The product was dried, concentrated and purified by precipitation in cold DCM to obtain 6.2 g (yield ca. 78%) of a white solid (HEOMC-PH).

¹H NMR (500 MHz, DMSO-*d*₆, ppm): δ 13.28 (s, 1H), 7.82–7.73 (m, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.65–7.61 (m, 3H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.20 (d, *J* = 1.3 Hz, 1H), 4.64–4.55 (m, 2H), 4.42–4.38 (m, 2H), 2.38 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆, ppm): δ 167.8, 167.5, 161.2, 160.1, 154.7, 153.3, 132.2, 131.9, 131.4, 131.1, 129.0, 128.2, 126.5, 113.3, 112.4, 111.3, 101.4, 66.3, 18.1. Electron-ionization mass spectroscopy (EI-MS): *m/z* calculated for C₂₀H₁₆O₇ [M + H]⁺: 368.0896, found: 368.0889. FTIR: ν (cm⁻¹) = 1719, 1675, 1614, 1394, 1285, 1269, 1213, 1134, 1075, 880, 675.

2.5. Synthesis of EVOH-HEOMC (ENH) copolymer

2.5.1. Modification of EVOH with p-nitrophenyl cloroformate: EN

EVOH was activated by following the procedure described by Sánchez-Chaves et al. [22]. Firstly, 5 g (135 mmol) of EVOH were dissolved in 170 mL of NMP at 80 °C in a double-walled reactor and then cooled to 0 °C. Afterwards, 9.3 mL (114 mmol) of pyridine and 23 g (114 mmol) of *p*-nitrophenyl chloroformate were added and stirred for 24 h. The modified EVOH was isolated by precipitation with ethanol and purified by reprecipitation from DMF in ethanol. Then, the product (EN) was dried at vacuum in the presence of phosphorous pentoxide to obtain a white solid with a substitution degree (SD) of 99%.

2.5.1.1. EN. ¹H NMR (DMSO- d_{6} , 500 MHz): δ 8.07 (s, 2H), 7.41–7.26 (m, 2H), 5.16–4.76 (s, 1H), 2.19–1.26 (m, 6H). ¹³C NMR (DMSO- d_{6} , 126 MHz): δ 155.1, 152.2, 144.9, 126.1, 122.3, 80.1, 78.1, 76.1, 74.4, 72.7, 37.8, 37.3, 33.6, 32.8, 28.6, 24.4, 20.1. FTIR: ν (cm⁻¹) = 3419, 2931, 1755, 1669, 1616, 1594, 1522, 1493, 1347, 1260, 1206, 1164, 1090, 1050, 1011, 858, 760, 722, 681.

2.5.2. Incorporation of HEOMC to EN

A mixture of HEOMC (10.6 g, 48.2 mmol) and TEA (10 mL, 72.3 mmol) was incorporated to a solution of EN (5.6 g, 24.1 mmol of reactive groups) in 280 mL of DMF. Catalyst DMAP (147 mg, 1.2 mmol) was added to the mixture and stirred 72 h at 70 $^{\circ}$ C. The solution was cooled at r.t. and precipitated over distillated water. The product was purified by precipitation from DCM in methanol to obtain 4.4 g of a light-yellow solid with a 62% of SD.

2.5.2.1. ENH. ¹H NMR (DMSO- d_{6} , 500 MHz): δ 7.59 (s, 1H), 6.89 (s, 2H), 6.13 (s, 1H), 4.89–4.62 (m, 1H), 4.44 (s, 2H), 4.31 (s, 2H), 2.35 (s, 3H), 2.07–0.99 (m, 6H). ¹³C NMR (CDCl₃, 126 MHz): δ 160.8, 159.5, 154.3, 153.8, 152.5, 125.8, 113.1, 111.8, 111.0, 101.1, 66.1, 65.2, 34.5, 33.1, 28.4, 20.6, 17.5. FTIR: ν (cm⁻¹) = 2928, 1713, 1611, 1510, 1389, 1250, 1200, 1147, 1070, 1013, 989, 846, 784, 731, 704.

2.6. Synthesis of EVOH-SUCCINIC-HEOMC (ESH)

2.6.1. Modification of EVOH with succinic anhydride (ES)

In a two-necked rounded flask, 5 g (135 mmol) of EVOH were dissolved in 100 mL of DMSO at 80 °C. The mixture was cooled at room temperature and 14 g (151 mmol) of succinic anhydride, 10.6 mL (135 mmol) of TEA and 200 mg (1.6 mmol) of DMAP were added. The mixture was stirred for 5 days until it changed to dark and then was precipitated over distillated water and purified by precipitation from THF in hexane to obtain 12.4 g of a dark solid with SD of 89%. The modified copolymer was dissolved in 200 mL of THF to avoid the crosslinking.

2.6.1.1. ES. ¹H NMR (DMSO- d_6 , 500 MHz): δ 12.15 (s, 1H), 4.77 (s, 1H), 2.50–2.38 (m, 4H), 1.73 (s, 2H), 1.42 (s, 2H), 1.18 (s, 2H). ¹³C NMR (DMSO- d_6 , 126 MHz): δ 173.5, 172.3, 171.9, 67.1, 38.3, 37.9, 28.9, 25.2. FTIR: ν (cm⁻¹) = 2929, 1707, 1408, 1379, 1159, 992, 953, 828.

2.6.2. Incorporation of HEOMC to ES

7 g (80 mmol) of ES were previously dissolved in 70 mL of THF and were added to 250 mL of DMF. After that, 11.8 g (54 mmol) of HEOMC, 13.8 g (67 mmol) of DCC and catalyst DMAP were added to the solution under stirring at 60 °C for 48 h. Then, the mixture was cooled to room temperature, precipitated over distillated water and purified by precipitation from DCM in methanol. The modified copolymer was dried at vacuum to obtain 10.1 g of a white solid with a SD of 55%.

2.6.2.1. ESH. ¹H NMR (DMSO- d_6 , 500 MHz): δ 8.16 (s, 1H), 7.60 (s, 1H), 6.89 (s, 2H), 6.14 (s, 1H), 4.76–4.69 (m, 1H), 4.35 (s, 2H), 4.25 (s, 2H), 2.56–2.29 (m, 7H), 1.76–1.05 (m, 6H). ¹³C NMR (DMSO- d_6 , 126 MHz): δ 171.8, 169.4, 161.1, 159.9, 154.6, 153.1, 126.3, 113.2, 112.2, 111.2, 101.2, 66.4, 62.4, 32.4, 31.6, 30.1, 29.4, 29.1, 28.7, 28.5, 25.4, 25.1, 24.5, 18.0. FTIR: ν (cm⁻¹) = 2928, 2854, 1724, 1658, 1612, 1525, 1388, 1369, 1345, 1263, 1146, 1070, 1013, 986, 847, 808, 732, 704.

2.7. Synthesis of EVOH-PHTHALIC-HEOMC (EPH)

2.7.1. Modification of EVOH with phthalic anhydride (EP)

5 g (135 mmol) of EVOH were dissolved in 200 mL of DMF at 80 °C, the temperature was cooled down to 60 °C. Then, 16.8 g (113 mmol) of phthalic anhydride, 16 mL (113 mmol) of TEA and catalyst DMAP were added. After 2 h, the product was precipitated over distillated water and further purified by re-precipitation from a mixture of acetone/ methanol 1/1 over distillated water. A white solid was obtained and dried at vacuum (10.9 g with a substitution degree of 98%).

2.7.1.1. EP. ¹H NMR (DMSO- d_6 , 500 MHz): δ 13.09 (s, 1H), 7.72–7.32 (m, 4H), 5.27–4.95 (m, 1H), 2.00–1.18 (m, 6H). ¹³C NMR (DMSO- d_6 ,

126 MHz): δ 167.7, 166.7, 132.4, 131.6, 130.7, 130.3, 128.5, 127.7, 74.7, 71.4, 68.3, 37.0, 33.0, 28.9, 24.5, 24.2, 20.1. FTIR: ν (cm⁻¹) = 2928, 1701, 1599, 1579, 1283, 1261, 1127, 1070, 1039, 791, 742, 705, 676.

2.7.2. Incorporation of HEOMC to EP

In a two necked rounded flask, 5.5 g (45 mmol) of EP and 6.7 g (31 mmol) of HEOMC were dissolved in 125 mL of anhydrous DMF. In another flask, 6.3 g (31 mmol) of DCC and catalyst DMAP were dissolved in 20 mL of anhydrous DMF. The solution was incorporated over the first flask with a syringe and was stirred at 60 $^{\circ}$ C for 24 h. The solution was precipitated over distillated water; the solid obtained was dried with phosphorous pentoxide and purified by dissolution in DCM and precipitation over methanol twice. The white solid obtained was dried at vacuum (8.9 g with a substitution degree of 40%).

2.7.2.1. EPH. ¹H NMR (500 MHz): δ 7.97–7.11 (m, 5H), 6.84 (s, 2H), 6.09 (s, 1H), 5.47–4.75 (m, 1H), 4.71–4.03 (m, 4H), 2.25 (s, 3H), 2.05–0.25 (m, 6H). ¹³C NMR (DMSO, 126 MHz): δ 167.2, 166.6, 161.5, 160.4, 155.0, 153.1, 139.2, 131.8, 129.0, 126.7, 113.7, 112.7, 111.7, 101.6, 75.7, 72.9, 70.0, 66.7, 63.9, 34.0, 31.6, 30.5, 29.5, 26.0, 25.3, 24.4, 18.4. FTIR: ν (cm⁻¹) = 2929, 2855, 1713, 1650, 1613, 1512, 1448, 1389, 1367, 1345, 1259, 1135, 1068, 848, 770, 740, 706.

Finally, all materials were processed into films by compression molding in a hot press (Dr. COLLIN 200 \times 200) at 100 °C by using a film mold (50 \times 50 mm²). ¹H NMR and ¹³C NMR spectra are depicted in the Supporting Information (Fig. S1 to S17).

2.8. Characterization techniques

All molded compressed EVOH copolymers were elucidated by ¹H NMR and ¹³C NMR spectra at 500 MHz in a Varian System 500 spectrometer by using deuterated dimethyl sulfoxide (ca. 8% w/v). Fourier transform infrared (FTIR) spectra were acquired with a Spectrum One FTIR spectrometer with a resolution of 4 cm^{-1} and 16 accumulation scans (Perkin-Elmer Co., Norwalk, CT, USA) in the 4000-650 cm⁻¹ region at room temperature. The modification degree of EVOH copolymers was also confirmed by UV spectra recorded in a NanoDrop one (Thermo Fisher Scientific). Coumarin modified EVOH copolymers were irradiated at 365 nm with 5 imes 8 W 365 nm - UV lamps for 210 min to produce the coumarin [2 + 2] cycloaddition reaction, while they were irradiated at 254 nm with 5 \times 8 W 254 nm - UV lamps during 180 s for the photo-cleavage reaction. Thin copolymer films were casted over the external surface of a quartz cell and the UV spectra were acquired with a Perkin Elmer Lambda 35 UV/VIS spectrometer (Norwalk, CT, USA) from 400 to 200 nm. The yield of photo-dimerization reaction was obtained from the absorbance at 320 nm (A 320) using the Eq. (1) [23]:

Photo – dimerization (%) =
$$\frac{A \ 320_0 - A \ 320_f}{A \ 320_0} \times 100$$
 (1)

 $A320_0$ and $A320_f$ are the absorbance values measured at 320 nm before and after the irradiation at *t* time, respectively.

Glass transition (T_g) and melting (T_m) temperatures were determined by Differential Scanning Calorimetry (DSC). Measurements were performed with a TA Instruments DSC Q2000 (New Castle, DE, USA) under nitrogen atmosphere (50 mL/min). Samples were sealed in aluminum pans and heated from -80 to 100 °C at 10 °C/min. The degree of crystallinity (X_c) was calculated from the enthalpy of a 100% crystalline poly(vinyl alcohol) (PVA) (157.8 J/g) [24]. TA Instruments TGA Q500 thermal analyzer was used to perform the thermogravimetric measurements under dynamic mode using nitrogen atmosphere (flow rate of 60 mL/min). Samples were heated from room temperature to 700 °C at a heating rate of 10 °C/min. The initial degradation temperatures (T_0) were obtained at 5% of mass loss and temperatures at the maximum degradation rate (T_{max}) were obtained from the first derivative of the TGA curves (DTG). Microindentation measurements were obtained with a Vickers indentator attached to Leitz microhardness (MH) tester. Experiments were undertaken at 22 °C with contact load of 980 N and a contact time of 25 s. MH (in MPa) were calculated according to the relationship: MH = 2 sin 68 P/d [2], where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area.

Surface wettability of the films was obtained with a KSV Theta goniometer by static water contact angle (WCA) measurements in contact mode. The volume of the droplets was 7.0 μ L and the contact angle was determined as the average value of 4 drops of distilled water randomly deposited with a syringe the film surface. The surface of the films was observed by scanning electron microscopy (SEM) using a Philips XL30 microscope with an acceleration voltage of 25 kV. Prior to SEM observation, the films were coated with gold. Antifouling properties of EVOH derivatives were obtained by immersing the films $(1 \times 1 \text{ cm})$ in solutions 0.01 M of bovine serum albumin-fluorescein isothiocyanate conjugate (BSA-FITC) in Trizma hydrochloride buffer solution for 3 h at 25 °C. Then, the film was removed from the solution and the unbound protein concentration was analyzed in the resultant solution by fluorescence spectroscopy in a Synergy HTX Multi-Mode Reader spectrophotometer (Bio-Tek) at an excitation wavelength of 480 nm and an emission wavelength of 525 nm. Briefly, 100 µL of each solution was placed in a 96-well round-bottom microplate. All films were analyzed in triplicate, and blank experiments were also performed with the Trizma buffer solutions. The fluorescence intensity of each sample was measured and the data were converted to concentration of unbound protein using the corresponding standard curve. From this data, the amount of BSA-FITC adsorbed onto the surface of the film was calculated by subtracting the unbound concentration from the initial concentration and the represented in ng cm^{-1} .

3. Results and discussion

The different synthetic routes followed to obtain EVOH containing coumarin groups are represented in <u>Scheme 1</u>. Notice that although all the obtained coumarin derivatives presented similar coumarin group the chemical structure of the resulting copolymers significantly differs.

3.1. Characterization of the copolymer ENH obtained by route a

EN modified copolymer was characterized by FTIR, ¹H and ¹³C NMR. The most characteristic IR bands are shown in Fig. 1A. Coumarin presents typical absorption bands at 1720 and 1615 cm⁻¹, belonging to C=O and C=C lactone stretching vibration, respectively. The C-O ester stretching vibration band appears at 1278 and 1070 cm⁻¹ and C-H aromatic out of plane bending vibration appears at 840 cm⁻¹ [21]. The most characteristic signals of EVOH appear at 1440 cm⁻¹ (methylene asymmetric stretch), 1330 cm⁻¹ (methine asymmetric stretch), 1087 cm⁻¹ (C-O stretch) and 840 cm⁻¹ (deformation of C-H out of plane). The hydroxyl stretch (3320 cm⁻¹) and the methylene anti-symmetric stretch (2900 cm⁻¹) bands are not shown in the Fig. 1A.

Fig. 1B shows ¹H NMR signals of EN as well as those of HEOMC and EVOH. Aromatic signals of HEOMC appear at 7.7, 6.9, and 6.2 ppm, proton of hydroxyl group at 4.9 ppm, the methylene groups at 4.1 and 3.7 ppm and the methyl group at 2.4 ppm [13]. EVOH signals appear in three regions: from 4.1 to 4.7 ppm (hydroxyl groups), from 3.3 to 3.9 ppm (methine groups) and from 1.2 to 1.4 ppm (methylene groups) [22]. These three groups of alcohol and methylene signals correspond to the isotactic, heterotactic and syndiotactic arrangement in PVA [25].

The substitution degree (SD) of modified EVOH copolymers was calculated by using ¹H NMR. EVOH methylene signals (between 2.1 and 0.6 ppm) were compared with methine signal (around 4.5 ppm) of modified groups to determine the SD (Eq. 2) in the copolymer without coumarin (EN). As EVOH is a copolymer with 56% of vinyl alcohol, the methine signal is referred to 56 per each 100 repeating units. Besides, the methylene signal contains two protons, which correspond to vinyl

group (56%), and four protons of the ethylene (44%) that are considered in the equation.

SD(without coumarin) (%)

$$= \frac{Integral of methine at 4.5 ppm \times (2 \times 0.56 + 4 \times 0.44)}{Integral of methylene at 2.1 - 0.6 ppm \times 0.56}$$
(2)

The incorporation of coumarin to the EVOH copolymer is confirmed by ¹H NMR, ¹³C NMR and FTIR. In the Fig. 2 the most important ¹³C NMR and FTIR signals are shown. The presence of the carbonyl group in the copolymer ENH, belonging to the *p*-nitrophenyl chloroformate is confirmed by the signal at 154 ppm in the ¹³C NMR spectrum, as can be observed in the Fig. 2A and marked with a discontinuous blue rectangle. Carbonyl group can also be distinguished by FTIR with a shoulder at 1735 cm⁻¹ corresponding to the C=O stretching vibration (Fig. 2B). Also, the end of reaction can be followed by FTIR (Fig. 2B), where aromatic bands at 1520 and 1350 cm⁻¹ disappear (marked as blue discontinuous circles) and the coumarin lactone band at 1615 cm⁻¹ appears (marked as red discontinuous circle).

Meanwhile, in coumarin modified copolymers (ENH, ESH and EPH) the SD was calculated by comparison of the HEOMC aromatic signal at 6.1 ppm and the methine signal at 4.5 ppm of modified EVOH (Eq. 3). Therefore, the SD is referred to the amount of coumarin that has reacted with the modified EVOH.

$$SD_{(with \ coumarin)}(\%) = \frac{Integral \ of \ HEOMC \ at \ 6.1 \ ppm}{Integral \ of \ methine \ at \ 4.5 \ ppm}$$
(3)

3.2. Characterization of the copolymer ESH obtained by route B

The modification of EVOH with succinic anhydride (ES), and subsequently modification with HEOMC (ESH) were also confirmed by ¹H NMR and FTIR spectroscopy (see Fig. 3). Methine signals in EVOH (3.3 to 3.9 ppm) are shifted to 4.8 ppm when EVOH is modified with succinic anhydride (pictured with blue discontinuous circle in Fig. 3A). The incorporation of coumarin to ES (Fig. 3A) shifts the methylene bands of HEOMC at 3.7 and 4.1 ppm to 4.2 and 4.3 ppm in ESH (red discontinuous circle), respectively. In addition, the methine group at 4.8 ppm in ES is slightly affected by the incorporation of HEOMC and is shifted to 4.7 ppm in ESH. Similarly, the FTIR spectra confirmed the successfully modification of the EVOH copolymer, obtained by this route. In the FTIR spectra (Fig. 3B marked in blue characters), the appearance of the carbonyl stretching band belonging to the dimer C=O in carboxylic acids at 1710 cm⁻¹ and a shoulder of ester C=O stretch at 1725 cm^{-1} confirm the process [9]. In the FTIR spectra (Fig. 3B), the modification of ES with HEOMC induces the decrease of the C=O acid dimer band. Furthermore, the presence of C=O (1655 cm⁻¹) and C=C lactone (1615 cm⁻¹) bands of coumarin are marked in red; also a displacement in the C=O stretching from 1705 to 1655 cm⁻¹ is observed, triggered by hydrogen bond interaction with the carboxyl groups of unmodified ES.

3.3. Characterization of the copolymer EPH obtained by route C

Likewise, the introduction of phthalic anhydride and afterwards HEOMC into the EVOH copolymer was elucidated by ¹H NMR and FTIR spectroscopy. In the Fig. 4A the influence of the phthalic anhydride into the EVOH chain (EP) is shown by the presence of the methine band at 5.1 ppm and also the aromatic protons of phthalic ring between 7.3 and 7.7 ppm (marked a with discontinuous blue circle). Moreover, in the FTIR spectrum (Fig. 4B) the presence of carbonyl vibrational strength at 1705 cm⁻¹ is also marked.

The incorporation of HEOMC into the EP is also established by the presence of new aromatic signals of HEOMC in the ¹H NMR spectrum (marked with a red discontinuous circle in Fig. 4A). Moreover, the carbonyl vibrational strength of lactone coumarin bands at 1655 cm⁻¹



Scheme 1. Synthetic routes of modified EVOH copolymers.

(C=O) and 1615 cm⁻¹ (C=C) are observed (Fig. 4B).

The substitution degree of the copolymers EP and EPH were determined thought the (Eqs. 24), and results are collected in Table 1.

3.4. Photo-dimerization properties

Coumarin-modified EVOH copolymers were irradiated with a UV lamp to study the photo-dimerization reaction of coumarin in the different systems. The photo-dimerization process was estimated with UV–vis spectrophotometry by following the decreasing of the absorption band of coumarin double bond at 320 nm [21]. Likewise, the photo-cleavage process of the coumarin dimer triggers the increase of the same band. The photo-conversion degree of coumarin-modified EVOH copolymers is shown in Fig. 5. The higher photo-dimerization yields were obtained for the sample ESH, which is caused by a better mobility of coumarin moieties linked to the succinic chain extender. The results obtained for ENH and EPH are similar, with more rigid spacer groups. The photo-cleavage process is a faster route and is in equilibrium with other parallel reactions, i.e. asymmetric fragmentation [6]. The photo-cleavage process is highly influenced by the mobility and rigidity of coumarin moieties. Also, the photo-cleavage process in EPH is influenced by the absorption of phthalic ring at around 290 nm (see Fig. S18 in Supporting Information). In this case, phthalic ring can absorb energy at wavelengths close to those of coumarin



Fig. 1. FTIR (A) and ¹H NMR (B) spectra of: EVOH, EN and HEOMC.



Fig. 2. ¹³C NMR (A) and FTIR (B) spectra of: EVOH, EN, ENH and HEOMC.

dimer, avoiding a more efficient photo-cleavage [26].

The SD of coumarin modified copolymers was also calculated by UV spectroscopy in a Nano-drop and the Lambert-Beer's law (Eq. 4). The modified copolymers were dissolved in DMF and the absorbance of each sample was measured 4 times.

$$SD_{(UV)}(\%) = \frac{\frac{|Abs|}{\epsilon}}{C_i} \times 100$$
(4)

Where |Abs| is the average absorbance and C_i is the initial concentration of each sample. The absorption coefficient of HEOMC ($\epsilon_{320} = 14,226 \pm 211 \ \text{mol}^{-1} \ \text{L} \ \text{cm}^{-1}$), HEOMCO ($\epsilon_{320} = 11,184 \pm 517 \ \text{mol}^{-1} \ \text{L} \ \text{cm}^{-1}$) and HEOMC-PH ($\epsilon_{320} = 11,581 \pm 562 \ \text{mol}^{-1} \ \text{L} \ \text{cm}^{-1}$) were previously calculated in DMF. These results are in agreement with the NMR measurements. The compilation of all modified copolymers with molar ratio of each comonomer and the SD of coumarin are shown in Table 1.

It should be observed that SD values obtained by NMR and UV spectroscopy are very similar and, therefore, both techniques could be easily used to study coumarin-based systems.

3.5. Thermal properties

The thermal properties of modified EVOH copolymers were studied by DSC and TGA and their main results are summarized in Table 2.

The EVOH copolymer is composed of ethylene and vinyl alcohol units, with inherent capacity to form three-dimensional networks and with high crystallinity. Its corresponding transitions should appear between these two homopolymers. The DSC heating curve shows two thermal transitions in EVOH (see Fig. 6A); the glass transition of EVOH (T_g) that appears at 54 °C, and the melting of crystalline domains (T_m) , at 166 °C [27]. The enthalpy of this transition is 79.3 J/g, that corresponds to X_c of 50.3%, which is in the range of this copolymer at the performed conditions. Nevertheless, a total loss of crystallinity can be observed when EVOH is modified, provoked by the disruption of the crystalline order produced by the substituents [28]. The different series are also displayed in Fig. 6. When EVOH is activated with *p*-nitrophenyl chloroformate (Fig. 6B) presents higher stiffness due to the bulky substituent. Therefore, EN shows a higher Tg than EVOH, 67 °C. The incorporation of HEOMC leads to the elimination of nitrophenyl group and increase the flexibility; then, ENH displays a Tg at 44 °C. The introduction of coumarin leads to intramolecular interactions between themselves or with the free hydroxyl groups in EVOH [22]. In contrast, the chemical modification of EVOH with succinic anhydride (Fig. 6C) provokes a diminishment on the Tg from 54 °C to 11 °C. Succinic moieties provide higher mobility to the polymer matrix leading to a reduction of the $T_{\rm g}$ value and as happen with EN, its insertion inhibit the crystallization of EVOH [29]. The posterior incorporation of HEOMC to obtain ESH, gives as result a movement restriction due to coumarin moieties and then, the T_g rises up to 42 °C. Meanwhile, the modification with phthalic anhydride introduces more rigidity to EVOH, resulting in the highest value of Tg (81 °C) (Fig. 6D). Again, when HEOMC is incorporated to obtain EPH, this gives a slight flexibility even though its $T_{\rm g}$ is still high, 72 $^\circ C$ in part due to its smaller modification degree.

In order to analyze the thermal stability of EVOH copolymers, TGA measurements were performed. Weight loss and DTG results are shown in Fig. 7. It is well-known that polyethylene acts as a thermal stabilizer



Fig. 3. ¹H NMR (A) and FTIR (B) spectra of: EVOH, ES, ESH and HEOMC.



Fig. 4. ¹H NMR (A) and FTIR (B) spectra of: EVOH, EP, EPH and HEOMC.

in EVOH copolymers, therefore two peaks of maximum degradation temperature are shown in the DTG curves. The first one appears at 396 °C, corresponding to vinyl alcohol units, which matches with the PVA degradation [30]. The second peak at 444 °C corresponds to the ethylene degradation [31]. In general, the degradation starts at lower temperatures in modified EVOH copolymers. Nevertheless, the modification of the EVOH copolymer with coumarin induces higher maximum degradation temperatures corresponding to the ethylene degradation. This behavior could be ascribed to the antioxidant ability of coumarin [32], as it was already observed in other polymeric matrix such as $poly(\varepsilon$ -caprolactone) (PCL) [7]. This effect is especially marked in the sample ENH, which presents the higher value of T_{max} (462 °C) due to the higher amount of coumarin in this formulation (see Table 1 with the highest degree of substitution). It should be noted that the samples ESH and EPH show three degradation steps in the thermogram. The lower substitution degree in these copolymers when coumarin is incorporated leads to different interactions between structure of activator, unreacted hydroxyl groups and coumarin moieties.

3.6. Microhardness

The mechanical properties of coumarin-modified EVOH copolymers were studied by microhardness test to evaluate the elastic recovery or the resistance to deformation before and after photo-dimerization process. The polymer modification usually leads to an arrangement between the moieties, which can interact with themselves or show entanglements. This behavior produces a variation in the permanent plastic deformation at the surface of the polymeric film.

The MH results are shown in Table 3. In general, the increase in the MH is related with the entanglement of the modified chains, as well as the interactions between coumarin moieties. In the case of EVOH, the irradiation could produce a film annealing with an increase of crystallinity and higher rigidity. This fact is not possible in modified copolymers due to the absence of crystallinity. For that reason, it is expected that neat EVOH presents lower values of MH than modified copolymers. Additionally, ENH shows high MH values, which is similar to that of ESH and higher than that of EPH. These values are in concordance with the already commented restriction on the mobility of polymer chains, i.e. Tg (see Table 2) and the degree of coumarin incorporation. There are not significant variations in the MH with the irradiation process with the exception of the sample ESH, which shows the highest photo-crosslinking degree (75%) of coumarin. This behavior can be ascribed to the higher flexibility of succinic extender that favors the photo-dimerization process.

3.7. Surface wettability

The surface wettability of the coumarin-modified EVOH copolymers before and after UV irradiation process was studied by water contact angle. The results are also collected in Table 3 and can be considered as hydrophilic surfaces with contact angles lower than 90°. As expected, the irradiation of neat EVOH does not modify the surface, since it does not contain coumarin groups; however, a film annealing can be performed with an increase of crystallinity and higher rigidity, which is not significant to modify its water contact angle. The value of neat EVOH was in the range of already reported works of EVOH with 44% of ethylene content [33]. Generally, the hydrophilic behavior of EVOH is slightly increased when EVOH is modified with coumarin derivatives because the modification intercepts the inter- and intramolecular bonds between hydroxyl groups present in the vinyl alcohol fraction of EVOH [33], leaving free hydroxyl groups able to interact with water at the surface of the film and, thus, enhancing the surface wettability of the materials. This is the case of ENH with the higher modification degree with coumarin and free vinyl alcohol units. In the case of ESH and EPH, with lower modification degrees, the rest of vinyl alcohol units are capped with succinic and phthalic acid moieties, respectively. These groups could interact between themselves or be exposed at the surface, enhancing their wettability. The differences between ENH, ESH and EPH are not significant.

Additionally, SEM images are taken to analyze the surface since it is well-known that the roughness of surface can influence the contact angle [34,35]. It is observed in Fig. 8 that there are smooth and flat surfaces, therefore, the differences between them have to be due to the chemical structure.

Meanwhile, the photo-crosslinking process in EVOH copolymers bearing a coumarin moiety decreases the distance between hydrophobic groups in coumarin by forming the cyclobutane units [13] and it could induce to a less hydrophilic behavior in the coumarin-modified copolymers.

3.8. Antifouling properties

The protein absorption experiment was performed to study the antifouling properties of the resulting coumarin-modified EVOH copolymers before and after UV irradiation process. The samples with approximately 1 cm² of surface area were incubated into the bovine serum albumin solution. The results of BSA-FITC adsorbed mass per unit area, m_{ads} , are shown in the Table 3. The absorption of BSA onto the surface of the film is related with their hydrophobic performance [36]. Generally, the absorption of BSA onto the surface of the copolymers is reduced when EVOH is modified with coumarin [18]. In effect, from the

Table 1

Molar ratio and substitution degree of coumarin in EVOH copolymers.

Structure	Name	х	у	z	SD _{NMR} (%)	SD _{UV} (%)
$ \begin{array}{c} \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	EN	0.01	0.55	-	99 ± 5	-
$ \begin{array}{c} \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	ENH	0.21	0.35	-	62 ± 5	56 ± 2
$ \begin{array}{c} \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	ES	0.06	0.50	-	89 ± 5	
$\begin{array}{c} & & & \\ & & & \\ & & & \\ HO \end{array} \\ HO \end{array} \\ & & \\ HO \end{array} \\ O = \\ O $	ESH	0.05	0.23	0.28	55 ± 5	61 ± 7
$ \begin{array}{c} & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & $	EP	0.01	0.55	-	99 ± 5	
HO HO HO HO HO HO O HO O HO O O O O O O O	EPH	0.01	0.33	0.22	40 ± 5	39 ± 7

data collected in Table 3, it is clearly observed that the modification with coumarin enhances the protein-adsorption-resistance properties in EVOH modified copolymers. The amount of BSA adsorbed on the surfaces is much smaller in coumarin derivatives films that the protein adsorbed on EVOH. Moreover, the photo-crosslinking of coumarin seems to reduce even more the adsorption of BSA. This behavior may be due to different factors, including variation of the surface wettability

due to the changes in the chemical structure after photo-dimerization.

4. Conclusions

Coumarin moieties as photo-responsive segments have been successfully grafted to EVOH copolymers by activation with different chain extenders. Copolymers were characterized by FTIR, 1 H and 13 C NMR.



Fig. 5. Photo-dimerization and cleavage process of coumarin and conversion degree of coumarin-modified EVOH copolymers at different times of photo-dimerization (left side) and photo-cleavage (right side) processes.

 Table 2

 DSC and TGA thermal properties of coumarin-modified EVOH copolymers.

Sample	T _g (°C)	T _m (°C)	T _{onset} (°C)	$T_{max I}$ (°C)	$T_{max II}$ (°C)	T _{max III} (°C)
EVOH	54	166	329	396	444	-
EN	67	-	225	271	461	-
ENH	44	-	239	303	462	-
ES	11	-	220	283	322	460
ESH	42	-	216	196	340	457
EP	81	-	195	237	295	458
EPH	72	-	195	198	308	462

Standard error: Temperature \pm 1 °C.

The materials exhibited reversible photo-dimerization and photo-cleavage processes, whose conversion degree was conditioned by the nature of the chain extender. Thermal properties reveal that the modification induces to a complete loss of crystallinity and a significant alteration of the glass transition temperature. Likewise, coumarin triggered a higher thermal stability corresponding to the ethylene degradation of the final material. The photo-crosslinking produces a slightly increase of the hydrophilic behavior and also to render materials with enhanced antifouling properties. Therefore, the coumarin moieties grafted onto EVOH copolymers allowed to obtain interesting materials that could be capable to act as photo-responsive polymeric coatings with tunable hydrophilicity and antifouling performance by varying the chain



Fig. 6. DSC thermograms of all series of coumarin-modified EVOH copolymers. EVOH (A), ENH family (B); ESH family (C) and EPH family (D).



Fig. 7. Thermogravimetric analysis of all series: TGA (A) and DTG (B) of ENH family; ESH family (B, C) and EPH family (E, F).

Table 3							
Surface	properties	of	coumarin-modified	EVOH	copolymers.	The	irradiated
materials are depicted with "i-" before the name of the sample.							

Sample	MH (MPa)	WCA (°)	m $_{ads}$ (ng/cm ²)
EVOH i-EVOH ENH i-ENH ESH i-ESH	166 ± 10 188 ± 14 276 ± 2 266 ± 5 230 ± 5 232 ± 1 232 ± 1	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	75 \pm 1 75 \pm 2 19 \pm 1 n.d. 8 \pm 0 n.d.
EPH i-EPH	239 ± 2 235 ± 14	76 ± 5 83 ± 2	18 ± 0 48 ± 4

n.d. non detected adsorption.

extender used. These results suggest that both ENH and ESH copolymers achieved the greatest photo-responsive, thermal, mechanical and antifouling properties.

Data availability

The data that support the findings of this study are openly available in Digital.CSIC at https://digital.csic.es/.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 8. SEM images of all materials before and after irradiation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.reactfunctpolym.2020.104750.

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