Accelerated Weathering of Pectin/Poly(vinyl alcohol) Blends Studied by Spectroscopic Methods

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ABSTRACT: The blends of pectin (PEC) and poly(vinyl alcohol) (PVA) at different components ratios were prepared by mixing in water. Thin polymeric films of PEC/ PVA blends and pure polymers were obtained by casting method. All samples were then artificially aged using Suntest apparatus (Atlas) up to 780 h. The changes in chemical structure during sample ageing have been monitored by infrared and ultraviolet-visible absorption spectroscopies. The first stage of weathering (up to ~ 300 h) was very slow and alteration of chemical structure was negligible in all samples. Prolonged ageing (>300 h) caused more significant degradation processes. FTIR spectra exhibited the highest changes in hydroxyl and carbonyl

INTRODUCTION

The new biodegradable materials for special application in medicine, pharmacy, cosmetics, and food industry are presently very much needed. Blending of synthetic polymers (getting from petrol) and biopolymers (from renewable resources) can lead to obtain novel materials with desired properties, completely different than those for virgin components. However, improvement of some features accompanies the unexpected deterioration of another. It happens very often that combined properties are not additive.

Biodegradable packaging foils are still not used at sufficient level and the researchers make the great efforts to elaborate the production methods of environmentally friendly systems with high quality properties. Each proposed material should be well characterized and the impact of new products on the environment has to be also assessed.

The promising material for packaging industry, cosmetic, and pharmaceutical application is pectin natural polysaccharide originating from cell walls or intercellular regions of various plants. During the band ranges indicating the efficient photooxidation of macromolecules. The mechanisms of the observed processes have been discussed. It was found that PVA undergoes faster photoxidative degradation than pectin aged at the same conditions. The PEC/PVA blends exhibited the improved resistance to weathering comparing with both polymers aged individually. Mutual stabilization effect can be explained by intermolecular interactions between PEC and PVA confirmed by spectroscopic methods. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1936–1945, 2011

Key words: pectin; poly(vinyl alcohol); polymer blends; weathering; FTIR; UV-Vis spectroscopy

last two decades, the intensive studies concerning pectin characterization by numerous analytical techniques supplied relevant and useful information on its organization and behavior.^{1–8} The complicated chemical structure of pectin, strongly dependent on the type of raw material (including plant species) and conditions of extraction process, determines the mechanical and rheological properties of pectinbased materials as well as their gelation ability.

Particular nanostructure of pectin can be visualized by Atomic Force Microscopy.^{9,10} It was demonstrated that the native pectin forms the network containing rods, segmented rods, and kinked rods. In well organized structure, the uniformly distributed strands, pores, aggregates and junctions were observed. The AFM imaging of pectin gels allowed to explain the role of hydrogen bonds and hydrophobic interactions in network formation.

The properties of pectin are often modified by plasticization or blending with other synthetic and natural polymer.^{11–15} For instance, pectin/starch blends form edible films with good oxygen barrier properties which are important in preservation and protection of food articles.¹² These nontoxic, inert blends undergo enzymatic hydrolysis, thus, found also application as controlled drug delivery systems.¹³

Other example of materials based on pectin are blends with poly(vinyl alcohol), PVA.^{14,15} Owing to water-solubility, those blends can be recommended

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for production of detergents packages or temporary protective coatings. It was reported that pectin and poly(vinyl alcohol) are miscible in all ratios of components.¹⁵ The addition of PVA to pectin improves the toughness and decreases the brittleness of films.¹⁴

Pectin blended with chitosan¹⁶ or copolymer of lactide and glycolide¹⁷ is also destined to biomedical applications (drug release or tissue regeneration). Moreover, the mixture of two mentioned above polysaccharides: chitosan and pectin form polyelectrolyte complex membrane.¹⁸ This membrane, thermally crosslinked, becomes very stable in strongly acid and basic environment, additionally, it exhibits the reduced swelling due to conversion of salt bonds into amide bonds.

Recently studied ternary films of chitosan/poly (vinyl alcohol)/pectin exhibited antimicrobial activity against pathogenic bacteria, therefore, they were recommended for packaging of alimentary products.¹⁹

Modification of pectin by nanofillers such as montmorillonite or zinc oxide has been also reported.^{20–22} The formed nanocomposites were characterized by improved elastic modulus, thermal stability as well as gas and water vapor permeability.

Pectin-based blends with good mechanical properties were prepared in laboratory conditions by casting (usually from aqueous solutions) as well as by extrusion—method more important from technological point of view.^{23–25}

The review of recent literature indicates that investigations have been focused mainly on the biodegradation of PVA and pectin,^{26,27} while the effect of UV-radiation on stability of these polymers is less studied.

The submitted work concerns the investigations on weathering of pectin/poly(vinyl alcohol) blends (PEC/PVA) in artificial, accelerated conditions using SUNTEST apparatus. The PEC/PVA photostability, important in the case of outdoor application (e.g., as packaging materials or protecting coatings), can not be predicted on the base of behavior of pristine polymers.

The photodegradation of pectin composites upon high energy radiation (wavelength of 254 nm) has been described.^{28,29} Presented studies clarify the effect of radiation simulating natural sunlight for a PEC/PVA films.

EXPERIMENTAL

Materials

Pectin, PEC (ς -Aldrich), containing 87.6% of polygalacturonic acid (value given by producer) was produced from citrus fruits. The amount of methyl esterified groups in pectin was estimated by FTIR spectroscopy.

Poly(vinyl alcohol), PVA (hydrolysis degree: 98%, average molecular weight: 85,000–146,000 g/mol)

was also obtained from *ς*-Aldrich company. Content of residual acetic groups in PVA was evaluated by titration of acetic acid, evolved during hydrolysis, using NaOH solution.

Film preparation

Both polymers were dissolved in distilled water at elevated temperature (50°C). The polymeric blends were prepared by mixing PVA and pectin solutions (2% wt) in proper ratios.

Thin films of PVA, pectin and their blends of different compositions (70/30, 50/50, 30/70 wt %) were obtained by casting the solution directly onto spectrophotometric windows (of CaF_2 for FTIR and of quartz plates for UV-Vis analysis). After evaporation of the solvent, the samples were dried in vacuum at room temperature to a constant weight.

For spectroscopic measurements samples with the same thickness were chosen.

Weathering conditions

For artificial weathering, Suntest XLS device (Atlas), equipped with xenon lamp was used. Light was cut off by 290-nm filter made from borosilicate glass. The samples were put always in the same place and in the same order in the Suntest and irradiated in dry air without rotation. Following ageing cycles have been applied: 10 h of exposure followed by 10-h dark period (simulation of night).

The light intensity of 250 W/m^2 was kept; black panel temperature was 35°C. The rain simulation was not applied because both polymers are water soluble; moreover, in wet atmosphere, the pectin biodegradation starts immediately. Total amount of cycles was 39 (780 h), which correspond to radiation dose of 351 MJ/m². The test conditions were programmed.

The samples were taken out from Suntest after each cycle for spectroscopic analysis and again placed to proceed the ageing.

Tests for all specimens have been processed three times and obtained values were averaged.

Spectrophotometric analysis

UV-Vis spectra were performed on UV-PC 1600 spectrophotometer (Shimadzu, Japan) in 200–800 cm⁻¹ range. Besides of normal absorption curves— $A = f(\lambda)$, the differential spectra— $d^2A/d\lambda^2$ as a function of wavelength were obtained.

Infrared spectra in 400—4000 cm⁻¹ range were recorded with Genesis II FTIR Spectrophotometer (Mattson, USA) by collecting 64 scans. The resolution was 4 cm⁻¹. The integral intensities of bands (peak areas) and the difference (subtraction) spectra, A(t) - A(0), were obtained using a WINFIRST 3.57 software supplied by Mattson Instruments. A(0) and A(t) is absorbance of unexposed sample and absorbance after *t* hours of ageing, respectively.

Degree of methoxylation (MD) of pectin has been calculated as integral intensity (area) of band attributed to methyl esterified carboxylic groups (A_{1739}) divided by the sum of areas of ester and carboxyl bands ($A_{1739} + A_{1612}$) based on previously reported FTIR method^{8,30}:

$$\mathrm{MD}(\%) = \frac{A_{1739}}{A_{1739} + A_{1612}} \ 100\%$$

RESULTS AND DISCUSSION

General remarks

Prepared films of pure pectin and its blends with PVA were somewhat turbid in spite of filtration and centrifugation of solutions applied for film preparation. It suggests that the colloidal solution is formed. Moreover, partial immiscibility of blend components can occur, although the hydroxyl groups are present in each unit of pectin and PVA. The presence of OH groups in both components leads to hydrogen bonds formation, which usually facilitates the miscibility. Anyway, pectin belongs to polysaccharides family and has very complex structure.^{2,4-7} Besides of hydroxyls, other functionalities such as acetyl, metoxyl, carboxyl groups are present in this multiblock biopolymer. It was reported that pectin is composed of even 17 different monosaccharides, thus, some structural irregularities, numerous branching and sterical hindrances impede the full pectin miscibility with PVA at molecular level.

UV-Vis spectroscopy

The electronic absorption spectra of all studied samples are shown in Figure 1(a). Pectin exhibits characteristic band with maximum at 282 nm and low intensive branch absorption at 350 nm attributed to various chromophores (such as carbonyl groups which undergo $n \to \pi^*$ and $\pi \to \pi^*$ transitions). PVA film practically does not absorb above 250 nm, which is obvious because of very high hydrolysis degree of rough polymer (it contains only about 2% of residual acetate groups). The blend spectra are superposition of components spectra, thus, the intensity of 282-nm band decreases with the increase of PVA content in the blend. Because of the complexity of the pectin structure, we can expect that observed bands are the result of absorption by all present functional groups. The Figure 1(b), in which the second-derivative spectra are shown, supports this

assumption. The mathematical differentiation of standard spectra (zero-order) is a simple procedure for obtaining more information from complex, unresolved bands. The derivative spectrophotometry is particularly useful for analysis of mixtures in which the detection of minor components is difficult or impossible.^{31,32} In this method the signals become more narrow, some of them undergo amplification. The minimum (negative band) at second-derivative spectrum corresponds to the maximum at zero-order spectrum. Additionally, two satellite positive smaller bands appear for the major single peak.

In our case, the strict number and kind of chromophores is unknown but the second-derivative spectrum $(d^2A/d\lambda^2)$ of origin pectin clearly indicates that at least five to six absorbing components are present contrary to the differential spectrum of non-aged PVA, where only two main components can be seen. The comparable shapes of the second-derivative spectra (as for pectin alone) are observed for PEC/PVA blends, but the intensities of bands are apparently lower.

The examples of changes in electronic spectra after sample ageing are shown in Figure 2. In the spectra of pectin and its blends, the decrease of main band intensity and small changes in its position (from 282 to 278 nm) are observed up to 400 h. The decrease of absorbance is an evidence of polymer photolysis (or removing of chromophoric impurities) while the bands shift indicates the intermolecular interactions.

After the long-time weathering (>400 h) the gradual increase of absorbance in whole measurement range was observed in two samples: PVA [Fig. 2(e)] and 30/70 PEC/PVA blend [Fig. 2(d)]. The different behavior of these samples can be explained by the lack of chromophores in virgin PVA (only small amount of residual acetate groups exists in PVA, contrary to pectin macromolecules). However, PVA can undergo photoelimination leading to double bonds formation, similarly as other vinyl polymers exposed to UV.

The small rise of absorbance in remaining samples was found only in 240–290 nm range. It can be assigned to the formation of new chromophores (e.g., oxidized groups or unsaturated bonds, which are probably conjugated).

Generally, the alteration in UV-Vis spectra are negligible, however, the calculated relative changes of absorbance, allow for comparison of samples of different composition. In Figure 3 the changes of absorbance at 282 nm, expressed in percentages, are presented for all samples after 400 and 780 h ageing.

Unexpectedly, good photostability of 50/50 PEC/ PVA blend suggests that such composition facilitates intermolecular interactions enhancing the blend structure, contrary to the samples with prevailing amount of one component where the interactions



Figure 1 Electronic absorption spectra of pectin, poly(vinyl alcohol) and their blends with three different compositions (a), second-derivative spectra of the same specimens (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between homopolymer molecules are dominant. It means that in well mixed, entangled chains of both polymers, processes of energy transfer and its dissipation are facilitated. This way, the harmful radiation is not consumed in chemical reaction leading to material deterioration.

FTIR analysis

Non-aged samples

FTIR spectra of untreated samples in 800–3800 cm⁻¹ range are presented in Figure 4. The broad hydroxyl band with maximum at about 3400 cm⁻¹ and complex band at 2800–3000 cm⁻¹ attributed to the stretching vibrations of CHin the ringsand CH₃ in the methoxyl groups exist in all spectra.

The pectin spectrum exhibits additionally the strong absorption at 1739 and 1612 cm⁻¹ due to the methyl esterified moieties (-COOCH₃ stretching vibrations) and free carboxyl groups, COOH, respectively.^{18,33–36} These both bands were applied for determination of the methoxylation degree (MD), which, for native, non-aged pectin is equal to 27.8%.

Weaker bands that appear near 1437, 1327, and 1231 cm⁻¹ can be assigned to C–O–H (bending in plane) and C–H (wagging) vibrations. Few peaks at

1000–1200 cm⁻¹ (main maxima: 1099 and 1021 cm⁻¹) are related to C—O—H side groups, glycosidic bonds as well as C—O—C in saccharide rings (stretching vibrations).

The same bands are observed in the pectin blends. The carboxylate absorption (1612 cm⁻¹) decreases with the decrease of pectin content in the blend. It confirms previous statement that this band is particularly useful for estimation of content of polygalacturonic acid, which is the main component of pectin.³⁴

The spectrum of neat PVA also exhibits the clear carbonyl band located at 1731 cm⁻¹ although the amount of residual acetate groups in this polymer is low (only 2 wt%). The other characteristic bands appear at 1567 (weak), 1425, 1374, 1253 (C—H deformation vibrations) and 1092 cm⁻¹ (ether linkage).^{37,38}

The FTIR spectroscopy supplies an additional information about the intermolecular interactions between both polymers. In our case only small band shifts of a few cm⁻¹ have been found in the blend spectra comparing to the spectra of individual components. The position of these bands is also similar for aged specimens. The possible interactions between PVA and pectin molecules are shown in Scheme 1.

Aged samples

The effect of irradiation by xenon lamp in Suntest on chemical structure of the samples has been observed by FTIR. Figure 5 presents the difference spectra of pectin, PVA, and PEC/PVA blends after 400 and 780 h of ageing.

At the beginning of ageing (approximately up to 200 h), the changes in spectra are very low and irregular. Small decrease of intensity of hydroxyl band indicates that water (nonremoved during vacuum drying) adsorbed in polymers, is gradually evolved. Simultaneously, also carbonyl impurities or substituents weakly bonded to macrochains (so-called structural defects) are removed in this initial step (it is observed as a decrease of intensity of band at 1500–1800 cm⁻¹ range).

Prolonged weathering leads to more efficient oxidation of all samples, which is clearly seen in kinetic curves obtained on the base of calculated integral intensities of OH and C=O bands (Fig. 6-8), which are in detail discussed below.

Changes in hydroxyl range $(3000-3600 \text{ cm}^{-1})$

In FTIR spectra of pure PVA and pectin, the significant rise of the absorption of hydroxyl groups has been found after longer irradiation time (Fig. 6). Notwithstanding, PEC/PVA blends are characterized by lower yield of oxidation leading to OH groups formation. It



Figure 2 The comparison of UV-Vis spectra of nonaged (0 h, black) and aged (400 h, blue; 780 h, red) samples: pectin (a), pectin/PVA—70/30 (b), pectin/PVA—50/50 (c), pectin/PVA—30/70 (d), and PVA (e); to see color figures, the reader is referred to the web version of this article. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

suggests the mutual stabilization of both polymers. However, a definite conclusion can not be drawn because both pectin and PVA are very sensitive to atmospheric moisture. Even though precise, careful drying before experiment, the samples can physically adsorb water during ageing and aqutision of FTIR spectra. Anyway, the water plays an important role in biopolymers and in synthetic hydrophilic polymers.^{39,40} Owing to the possibility of the formation of hydrogen bonds between OH from macromolecules and H₂O, the particular structure is therefore enhanced.

Changes in carbonyl range (1500–1800 cm^{-1})

Carbonyl region in spectra of aged samples reveals that some new photooxidation products are formed

Journal of Applied Polymer Science DOI 10.1002/app

(Fig. 5). It should be noted that bands attributed to groups existing in virgin polymers overlap the bands of new formed moieties.

In pure pectin, these bands appear at 1728 and 1605 cm^{-1} , wherein first one increases slower than second one. It leads to the drop of methoxylation degree (MD) in pectin during 200–500 h of ageing [Fig. 5(a)]. One can conlude that abstraction of side groups (OCOCH₃ and COOH) competes the oxidation with formation of new oxygen containing moieties. The observed decrease of MD up to 500 h suggests that elimination of ester groups (Scheme 2, Reaction 1) prevails the abstraction of carboxyl subsituents (Scheme 2, Reaction 2). Longer degradation (600–780 h) practically does not change the MD in aged pectin.



Figure 3 Relative changes (%) of absorbance at 282 nm in: pectin (1), 70/30 PEC/PVA (2), 50/50 PEC/PVA (3), 30/70 PEC/PVA (4), and PVA (5) after 400 h and 780 h of ageing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2 presents main primary reactions caused by light in pectin. Additionally, the hydrogen abstraction as well as Norrish Type I and II processes, typical for carbonyl compounds, also appear. All free radicals formed in primary reactions can react with atmospheric oxygen and initiate the secondary processes. The propagation step can be repeated many times before free radicals deactivation (e.g., recombination or disproportionation).

The changes in the carbonyl region for aged PVA are also distinct. The new complex band with maxima at 1709, 1649, and 1597 cm⁻¹ is observed in difference spectrum [Fig. 5(d)]. These overlapped bands can be assigned to ketonic, aldehydes, and carboxylic groups formed during PVA photoageing (Scheme 3).

The mechanism of photooxidative degradation of PVA has been reported elsewhere.⁴¹ It should be noticed that mainly carbonyl residual groups in PVA are responsible for the light absorption. Excited C=O groups can transfer energy to other sites in macromo-

lecules, resulting of which primary reactions occur (Scheme 3, Part I). Ones radicals formed, participate in the secondary processes leading to various oxidized products and chain unsaturations. Photoproducts for aged PVA are shown in Scheme 3, Part II.

The development of carbonyl band in the spectra of aged blends is relatively slow and less efficient than that in pectin and PVA alone. Probably some interactions between functional groups (mainly hydroxyls) from pectin and PVA (Scheme 1), replacing the interaction between the same molecules, are responsible for partial improvement of resistance to weathering.

The changes of esterification degree of pectin in the degraded blends can not be simply determined by the same way as in pectin because the residual acetate groups from PVA absorb in the same region, thus, the MD would be over-estimated. On the other hand, the calculated ratio of 1739 cm⁻¹ band area to the sum $A_{1739} + A_{1612}$ is approximately constant in aged 70/30 PEC/PVA blend. However, the blend with major amount of PVA (70 wt%) exhibits the difference spectra more similar to PVA alone. In the time of 200–400 h ageing, the decrease of carbonyl band (observed as negative changes on difference



Scheme 1 Examples of possible interactions between pectin and PVA functional groups.



Figure 4 Fourier transform infrared spectra (non-normalized) of pectin, PVA and their blends in $800-1800 \text{ cm}^{-1}$ region; values of wavenumbers concern pure pectin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 5 The difference FTIR spectra of pectin (a), 70/30 PEC/PVA (b), 50/50 PEC/PVA (c), 30/70 PEC/PVA (d), and PVA (e) after 400 h (red line) and 780 h (black) ageing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 6 The relative changes of hydroxyl groups amount in pectin, poly(vinyl alcohol), and their blends versus ageing time (from FTIR). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2 Photoinduced side groups abstraction (1-3) and main chain scission (4) in pectin.

Journal of Applied Polymer Science DOI 10.1002/app



Scheme 3 General mechanism of PVA photodegradation (I, primary degradation products; II, secondary degradation products).

spectra is typical, while after weathering continuation (>500), fast oxidation occurs in these both samples [Fig. 5(d,e)].

The mechanism of photoreactions in the blends should include the photo processes characteristic for both polymers. Some reactions in PEC/PVA blends undergoing after photochemical initiation and free radical creation in PVA are shown in Scheme 4. Simultaneously, the free radicals formed in pectin molecules can also generate the reactions in the blend components (nonshown). As one can expect, besides of modification of polymeric chains, the lowmolecular weight degradation products appear too.

For the comparison of the behavior of blends with different composition the relative changes of total amount of carbonyl groups were calculated and plotted versus ageing time (Fig. 7). It can be concluded that the most efficient photooxidation takes place in PVA, whereas the most resistant is 50/50 PEC/PVA.

When the changes of total amount of carbonyl groups are plotted versus sample composition, the deviation from additivity rule is clearly seen (Fig. 8). The improvement of photostabilization (resistance to weathering) in the blend, with respect to pure polymers (i.e., pectin and PVA aged separately) is observed. As it is earlier suggested, it can be explained by intermolecular interactions, confirmed by the small shifts of absorption bands position in the blend spectra.

Changes in ether groups range (900–1200 cm^{-1})

This so called "finger print region" is characteristic for each type of organic compounds. The intensive absorbance in this region is characteristic for ether (C-O-C) groups: both glysocidic and in the ring structure of pectin molecule. Also PVA exhibits strong absorption in this region due to C-O-H vibrations.

Journal of Applied Polymer Science DOI 10.1002/app



Scheme 4 Rections in pectin in the presence of PVA (R - photochemically induced radical in PVA e.g., HO, CH_3 , $O=C-CH_3$, etc.).

The relative changes in C—O content as a function of ageing time gives the same trend (nonshown) as observed for carbonyl kinetic curves (Fig. 7).

It is rather obvious because oxidized macrochains are reach in C—O—C and C—O—H bonds. In aged polymers, the competitive reactions take place: abstraction of side substituents followed by oxidation leading to new functional groups creation. Thus, one type of groups are replaced by others and finally the amount of photooxidation product increases.

CONCLUSIONS

The pectin, poly(vinyl alcohol) and their blends are relatively stable for ageing in accelerated conditions up to about 300 h, which was proved by FTIR and UV-Vis spectroscopies. In this first period, mainly the slow photolysis of macromolecules takes place. The changes of methylation degree in pectin indicate that the elimination of methoxyl groups are faster than the abstraction of carboxyl groups at the beginning of ageing. Contrary to carboxylic ones, these groups are probably not involved in hydrogen bonding.

The longer weathering (>300 h) causes more efficient photochemical oxidation in both polymers and their blends. It was found that PVA is more susceptible to photooxidative degradation than pure pectin and PEC/PVA blends.

The lower photosensitivity of pectin (comparing to PVA) can be explained by its complex structure and the possibility of energy transfer between various functional groups. The electron exchange excitation transfer is a very fast process, thus it competes with chemical reaction (bond breaking), which usually needs the longer excitation time.⁴² Therefore, the physical processes of energy dissipation in pectin take part in the stabilization of macrochains.

The proposed mechanism of blend photodegradation includes the abstraction of side constituents from polymeric chains and oxidation leading to the formation of various functional groups.

FTIR and UV-Vis spectroscopic methods, used for monitoring of the photodegradation progress, indicate also that some intermolecular interactions (hydrogen bonds, dipole–dipole type) between pectin and PVA macromolecules appear. Their strength depends on many factors: sample composition, accessibility, and circumstances around the functional groups, steric hindrances, macromolecules flexibility, etc. These interactions are crucial for the improvement of resistance against the blends ageing. The retardation effect of hydrogen bonds on photodegradation has been found in other polymeric blends.⁴³





Figure 7 The relative changes of total carbonyl group amount in pectin, poly(vinyl alcohol), and their blends versus ageing time (from FTIR). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 The relative changes of total carbonyl group amount in: pectin (1), 70/30 PEC/PVA (2), 50/50 PEC/PVA (3), 30/70 PEC/PVA (4), and PVA (5) after 400 h and 780 h of ageing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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Because the course of photochemical reactions depends on the blend composition it is therefore the appropriate choice of component ratio that makes it possible to control the degradation kinetics.

This study shows that PEC/PVA blends have sufficient photostability for outdoor applications and storage.

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