

HYDROHYPROPYL CELLULOSE/POLYURETHANE BLENDS. THE BEHAVIOR AFTER ACCELERATED AGEING. A FTIR STUDY

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*This paper is dedicated to the commemoration of the 100th birth anniversary
of Academician Cristofor I. Simionescu (1920-2007)*

A series of hydroxypropyl cellulose/polyurethane blends (PU_HPC 20/80, PU_HPC 50/50 and PU_HPC 80/20) were investigated by FT-IR spectroscopy after exposure to simulated ageing conditions (UV irradiation, 40 °C and 60% humidity) for 600 h. The degree of structural organization was analyzed through quantitative determination of the crystallinity indexes: total crystallinity index (TCI), lateral order index (LOI) and the hydrogen bond intensity (HBI), as well as by the evolution of the “ordered”, “disordered” and “free” areas in the carbonyl (1600-1800 cm⁻¹) spectral region. The accelerated weathering conditions determined structural modification in the PU_HPC blends in correlation with their composition and the exposure time, both polymeric components being affected by the hydrolysis and oxidation processes.

Keywords: hydroxypropyl cellulose, polyurethane, polymeric blends, aging, FTIR spectroscopy

INTRODUCTION

Cellulose and its alkyl substituted derivatives, such as hydroxypropyl cellulose (HPC) and hydroxypropyl methyl cellulose (HPMC), are promising polymers extensively applied in different areas: coating and building materials (enhancing mechanical and thermal properties), matrix for drug delivery (conferring biodegradability), blood purification membranes (due to their barrier properties), stimuli-responsive systems (due to their biocompatibility and biodegradability), antitumor, antimicrobial and antiinflammatory formulations (due to their non-toxicity), scaffolds for regenerative medicine, adhesives, cosmetics, *etc.*¹⁻³ HPC is a water soluble and biocompatible cellulose ether used as food additive, thickening or emulsifier and stabilizer.⁴ The application of HPC can be extended by physical or chemical cross-linking agents, such as polyalcohols, aldehydes,

carboxylic acids, *etc.*⁵ in order to improve their properties (swelling behavior in water for pharmaceuticals, film forming for ground covering, *etc.*), without altering the structure and function of the polymers themselves.⁶

Multi-component systems or blends based on cellulose derivatives are known for their application in pharmaceutical formulations for dosage of different soluble or insoluble drugs, hormones or enzymes.⁷ Blends of HPC or HPMC with acrylic acid or sodium alginate are applied as mucoadhesives, matrix for drug encapsulation and excipients with buccal and sublingual administration, or stable and non-irritant sustained release films.⁸⁻¹⁰ Another approach to improve the HPC physicochemical properties is blending with other natural or synthetic polymers, taking into account the mechanisms involved in polymer mixing, which can affect their final performance,

including mechanical properties, permeability, morphology and stability to degradation processes.¹¹ Generally, polymer blends may exist either as a completely homogenous phase structure or as segregated and distinct phases, the miscibility between the polymer components being dependent on the degree of association between polymers. Polymer blends between HPC and other natural or synthetic polymers can be obtained in different processing modes depending on the solvent, temperature, concentration, *etc.* – factors that directly influence the overall blend morphology and properties. Thus, blends of HPC with lignin, hyaluronic acids, polyethylene glycol, polypropylene glycol or polyurethanes can result as multiphase materials depending on the miscibility between them, which is studied by specific methods: viscosity, refractive index measurements, ultrasonic velocity, DSC, XRD, SEM or FTIR.¹²⁻¹⁶

Particularly, blends of cellulose derivatives with polyurethanes, possessing excellent mechanical characteristics, resistance to oil, grease and abrasion and very good processability, have been prepared for studying their stability and thermomechanical behavior,¹⁷ as well as their biodegradability under natural and simulated (accelerated) conditions,¹⁸ in order to predict the time of polymer durability, the behavior during ageing by monitoring the changes in physical and chemical composition mainly produced by hydrolysis and oxidation processing under UV irradiation and in moisture medium. Also, well-established ageing experiments (time, temperature, humidity, UV intensity and λ (nm) values) on cellulose-based materials can provide a good approximation of natural ageing.¹⁹⁻²⁰

Herein, we report on the ageing behavior of HPC/polyurethane blends in a simulated weathering environment (temperature, humidity and UV irradiation), considering the importance of these studies for the final application of these blends in outdoor conditions. We investigated the changes in the composition by using IR spectroscopy and we analyzed the chemical degradation reactions that may occur and the possible mechanisms of ageing in these blends.

EXPERIMENTAL

Materials

Klucel LF/Hydroxypropyl cellulose (HPC) with M_w of 95,000 Da was purchased from Aqualon (Hercules Inc., Wilmington, USA). Polyurethanes have been prepared by a reported procedure according to

ref.²¹ by using the following reagents: Pluronic L-61 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)) (Aldrich) with M_n of 2000 Da, PBA (Poly(butylene adipate)diol) (Aldrich) with M_n of 2000 Da, H₁₂MDI (methylene dicyclohexyl diisocyanate) (Aldrich) and sodium deoxycholate (SD) (Aldrich).

The polymeric films of PU, HPC and their blends (PU_HPC 20/80, PU_HPC 50/50 and PU_HPC 80/20) were prepared by the solvent casting method, as presented in ref.²¹ A schematic representation of the blends can be seen in Scheme 1.

Methods

Fourier transform infrared (FT-IR) spectroscopy

The infrared spectra were performed in the attenuated total reflectance (ATR) mode on a Bruker Vertex 70 spectrometer equipped with a ZnSe crystal accessory. A number of 32 scans at 4 cm⁻¹ resolution were applied to collect spectral data of the samples.

The overlapped and hidden peaks in the 1800-1600 cm⁻¹ and 1500-800 cm⁻¹ spectral regions were determined with the second derivative of the spectra. The calculated areas (with a 50% Lorentzian and 50% Gaussian function) of the peaks were used to determine the three standard crystallinity indexes reported in the literature: lateral order index (LOI), total crystallinity index (TCI) and hydrogen bonding intensity (HBI).^{22,23} The carbonyl region of the PU_HPC polymeric blends was deconvoluted by a curve-fitting method in order to determine the evolution of the “ordered”, “disordered” and “free” areas during the accelerated weathering process. OPUS 6.5 software was used to process the curve-fitting data. The procedure led to the best fit of the original curve with an error of less than 0.001.

Accelerated weathering

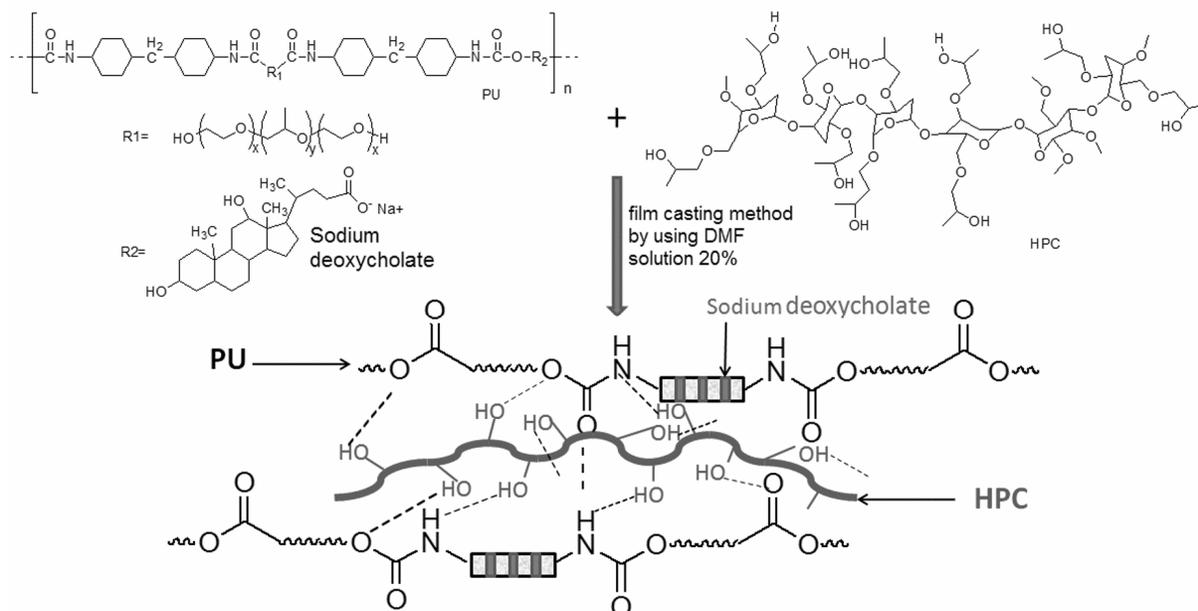
All the materials (blends and starting components) were aged in a laboratory chamber (Angelantoni Ind., Italy). The samples were exposed to the artificial light of a mercury lamp (200 < λ < 700 nm, incident light intensity 39 mWcm⁻²) at a temperature of 40 °C and 60% humidity. Samples were removed from the exposure chamber at set times (100, 200, 300, 400, 500, 600 h) and analysed; non-irradiated samples were used as reference.

RESULTS AND DISCUSSION

Accelerated ageing analysis is a useful method to appreciate and predict the long-term behavior of polymeric materials, because most polymers absorb UV radiations, which determine important modifications in their physical, mechanical and chemical structure. The accelerated weathering process also supposes the presence of higher temperature and moisture environment. The humidity can determine physical, photochemical or hydrolytic processes in polymer degradation,

but the main cause of degradation is oxidation, which may occur by the mechanism of

hydroperoxide formation, with generation of free radicals and propagation of chain reactions.²⁴



Scheme 1: Schematic representation of the PU_HPC blends

In the case of cellulose materials (considered photodegradable), two main reactions can occur under UV irradiation: hydrolysis (in glycosidic bonds) and oxidation (with generation of free radicals), which can affect the cellulose chains, producing cellulose yellowing (due to the formation of some chromophores, such as carbonyls and conjugated polyenes), and weakening processes. Although HPC has higher chemical stability and color modification is not so evident during accelerated ageing, as compared to other cellulose ethers, it possesses reactive hydroxyl groups, which are susceptible to oxidation, weakening the intermolecular interactions and reducing the strength of materials.²⁵

In the case of polyurethanes, depending on their composition, photooxidation can determine hemolytic scission in the urethane groups with generation of free radicals, followed by decomposition and recombination of the primary radicals, resulting in the formation of some secondary products (amino and carbodiimide structures and polycondensation of isocyanates).²⁶

In order to study the structural changes of the blends during weathering, FTIR spectra were registered after different weathering times (100 h, 200 h, 300 h, 400 h, 500 h and 600 h). The FTIR

technique is useful in the evaluation and quantification of both covalent and non-covalent interactions within HPC and the PU_HPC blends, allowing quantitative determination of crystallinity, expressed by crystallinity indexes.

Figure 1 shows the comparative spectra of the HPC and the PU_HPC blends during the accelerated weathering process. The IR spectra reveal the presence of a broad band at 3424 cm^{-1} assigned to O-H stretching vibrations, the characteristic bands attributed to the C-H asymmetric and symmetric vibrations at 2926 and 2856 cm^{-1} , C-O asymmetric stretches at 1050 cm^{-1} , while in the PU_HPC blends, the IR bands assigned to ester-urethane, carbonyl urethane ($\text{-N-H}\dots\text{O}=\text{C-}$), N-H bending, C-N stretching and C-O-C stretches can be observed at 1720 cm^{-1} , 1630 cm^{-1} , 1540 cm^{-1} and 1160 cm^{-1} .

During the ageing process, the intensities of O-H stretches and bending vibrations (at 1340 cm^{-1}) increase mainly due to the adsorbed humidity and the rearrangement in the hydrogen bonding. The position and the intensity of the other specific bands also change, highlighting that the humidity, temperature and UV irradiation affect the ratio between the crystalline and amorphous regions in the HPC and the PU_HPC blends.

By increasing of ageing period to 500 and 600 h, one can observe an intensity diminution of the

band at 2926 cm^{-1} and an increase in the intensity of the band at 800 cm^{-1} assigned to alkyl groups in the HPC and PU_HPC 20/80 blend. Also, in the IR spectra of the HPC and PU_HPC 20/80 blend, a redshift with 34 cm^{-1} of the band at 1060 cm^{-1} takes place, suggesting that degradation affects the C-O-C groups, while in the case of PU_HPC 80/20, a decrease in the intensity of the bands at 1070 cm^{-1} at 200 h of ageing and a blueshift of the band at 1168 cm^{-1} (specific to crystallized cellulose) after 300 h of ageing may suggest a cleavage of the glycosidic bond and degradation in the amorphous regions in HPC (Fig. 2).^{27,28}

The degree of structural organization was analyzed through quantitative determination of the crystallinity indexes: total crystallinity index (TCI), lateral order index (LOI) and hydrogen bond intensity (HBI),^{22,23} as the results of the ratio of the area corresponding to the bands: $\text{TCI} = (A_{1374}/A_{2920})$; $\text{LOI} = (A_{1416}/A_{904})$ and $\text{HBI} (\%) =$

(A_{3350}/A_{1337}) , and the results are presented in Table 1. The band at 1416 cm^{-1} in HPC and PU_HPC blends is associated with the amount of the crystalline structure of the cellulose chains, while that at 904 cm^{-1} corresponds to the amorphous region in HPC, the band at 1374 cm^{-1} is assigned to C-H bending mode, while the band at 2900 cm^{-1} is due to the C-H stretches.²² Also, taking into account the chain mobility and the bond distance, the determination of HBI (%) of HPC and PU_HPC blends is closely correlated with the organization in crystalline regions and evidences the degree of intermolecular regularity, as well as the amount of bound water, the bands at 1337 cm^{-1} and 3350 cm^{-1} being assigned to the O-H in-plane bending and O-H stretching vibrations, respectively.²⁹ The TCI and LOI indexes give information about the crystallinity degree and the overall degree of order in HPC and blends.

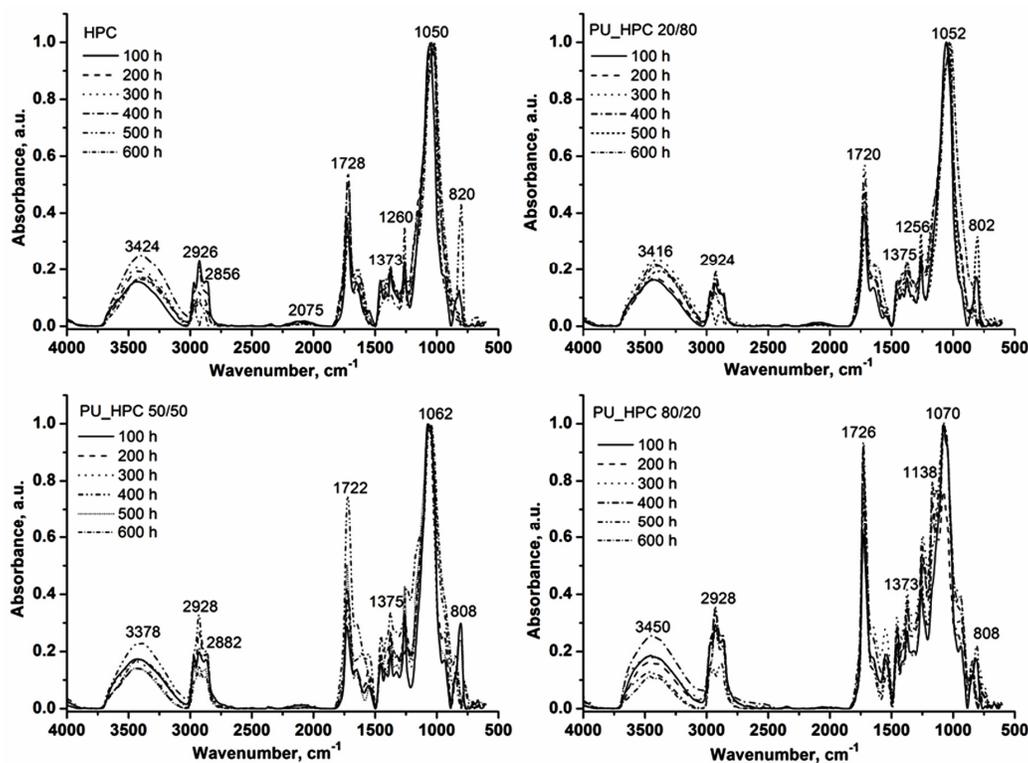


Figure 1: Comparative IR spectra of HPC and blends (PU_HPC 20/80, PU_HPC 50/50 and PU_HPC 80/20) during the accelerated weathering process

The changes in the area corresponding to the infrared absorption bands mentioned above determined non-uniform evolution of the crystallinity indexes at different exposure periods

under accelerated ageing conditions, highlighting that the mass loss occurring in the some ageing stages leads to molecular reorientation rather than

the loss of the amorphous regions in HPC and PU_HPC blends.

One can observe a stronger decrease in the TCI index at 100 h for HPC and at 200-500 h for PU_HPC 50/50 and PU_HPC 80/20, indicating that, upon blending with polyurethane 50% and 80%, the structural organization of HPC is affected (Table 1). The PU_HPC 80/20 blend has the lowest values for TCI (0.23) and LOI (0.43), also suggesting that an increased content of PU in the blends influences their degradability in the weathering environment. The presence of polyurethane in the structure of the blends

influences the overall degree of order, the LOI values increase especially after a long period (500 and 600 h) of ageing, suggesting that the release of some amorphous regions from the soft segments of PU results in an increase of crystallinity.³⁰ Also, the intensity of hydrogen bonds reflects the importance of the polyurethane component in the blends, the lowest values of HBI being present in the case of HPC and the PU_HPC 20/80 blend, suggesting that UV irradiation, temperature and humidity produce some structural changes in the structure of HPC by oxidative and hydrolytic processes.

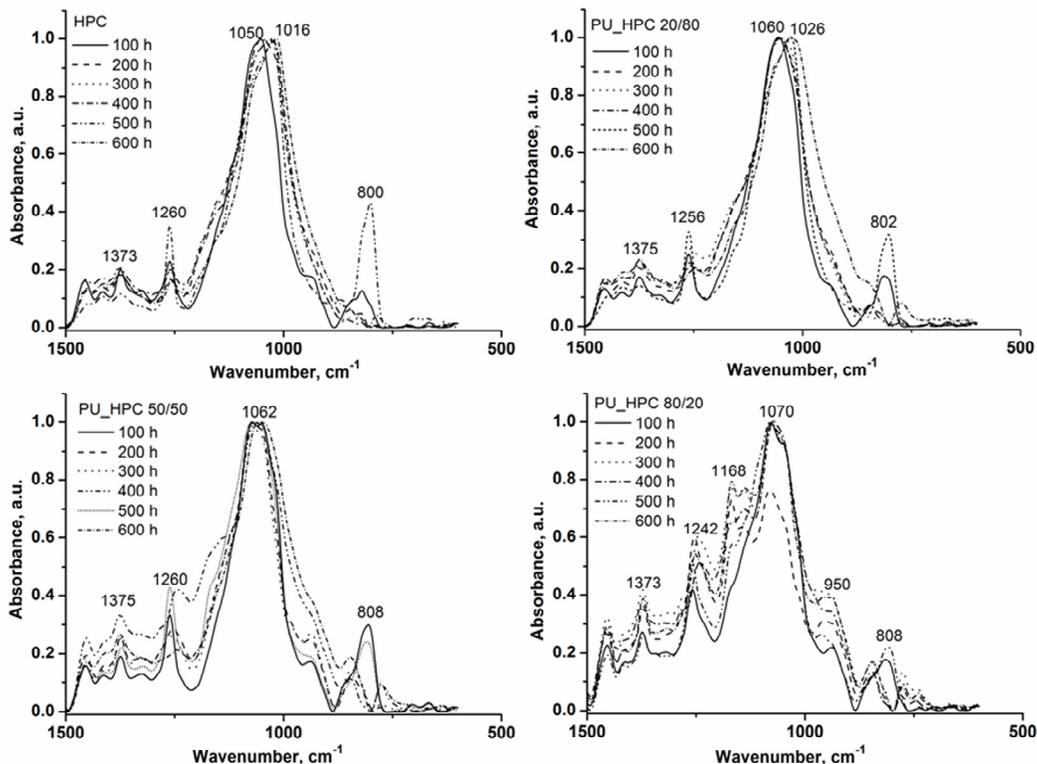


Figure 2: Comparative IR spectra of HPC and blends (PU_HPC 20/80, PU_HPC 50/50 and PU_HPC 80/20) during the accelerated weathering process in the 1500-500 cm^{-1} spectral range

Hydrolysis mainly causes the chain scission of HPC and soft segments in PU_HPC blends, generating carbohydrate fragments, diols and carboxylic acids, which promotes oxidations and hydrolysis cycles leading to autocatalytic degradation.³⁰ This process was evidenced by the detection of some specific absorption bands in the IR spectra of the PU_HPC blends in the carbonyl region (1600-1800 cm^{-1}). Thus, in the PU_HPC 20/80 blend, after 100-400 h of ageing, one can observe the appearance of new bands at 1744 cm^{-1} assigned to ester compounds, while at a higher

ageing period (500 h and 600 h), new bands appear at 1770 cm^{-1} , specific to hydroperoxides, suggesting that degradation mainly occurs by oxidative processes (Fig. 3). TCI and LOI indexes also increase for the PU_HPC 20/80 blends after 500 h and 600 h accelerated ageing, because of the reaction steps leading to breakdown of physical and chemical bonds between blend components during degradation.¹

In the blends with lower content of HPC (PU_HPC 50/50 and PU_HPC 80/20), degradation occurs especially by hydrolysis in the

ester groups, the deconvoluted IR spectra in the 1600-1800 cm^{-1} region revealing only the presence of some ester and carboxylic acid fragments (Figs. 4 and 5), and rarely by hydroperoxide radicals (PU_HPC 50/50 600 h).

The deconvolution of the IR spectra of PU and the PU_HPC blends in the carbonyl region (1600-1800 cm^{-1}) also allowed determining the influence of accelerated weathering on the hard segment of PU. This spectral region shows three major components highlighted by second derivative of

the spectra: “free”, hydrogen bonded “disordered” and hydrogen bonded “ordered” groups. Their corresponding position and area are presented in Table 2, while their evolution during the ageing process is shown in Figure 6. The analysis of the hard segment of polyurethane during accelerated weathering revealed a lower decrease in the hydrogen bonded ordered area and equilibrium between the free and hydrogen bonded disordered area.

Table 1
Calculated crystallinity indexes for HPC and PU_HPC blends

Sample	TCI (A_{1374}/A_{2920})	LOI (A_{1416}/A_{904})	HBI (A_{3350}/A_{1337}) (%)
HPC_initial	0.81	1.125	96.95
HPC_100 h	0.43	0.71	85.71
HPC_200 h	0.96	0.55	61.11
HPC_300 h	0.75	0.66	63.15
HPC_400 h	0.77	0.81	54.16
HPC_500 h	1.63	0.91	50.00
HPC_600 h	1.72	0.51	75.00
PU_HPC 20/80_initial	0.85	1.25	95.00
PU_HPC 20/80_100 h	0.49	1.33	83.22
PU_HPC 20/80_200 h	0.61	0.69	85.91
PU_HPC 20/80_300 h	0.96	1.18	59.32
PU_HPC 20/80_400 h	0.62	0.85	56.21
PU_HPC 20/80_500 h	1.16	1.14	52.06
PU_HPC 20/80_600 h	1.51	1.00	70.01
PU_HPC 50/50_initial	1.26	1.41	87.50
PU_HPC 50/50_100 h	0.38	0.74	75.00
PU_HPC 50/50_200 h	0.28	0.95	92.85
PU_HPC 50/50_300 h	0.34	1.17	93.33
PU_HPC 50/50_400 h	0.28	0.36	84.61
PU_HPC 50/50_500 h	1.22	1.21	92.16
PU_HPC 50/50_600 h	0.60	1.94	84.21
PU_HPC 80/20_initial	1.19	1.43	68.00
PU_HPC 80/20_100 h	0.28	1.70	85.00
PU_HPC 80/20_200 h	0.23	0.43	64.55
PU_HPC 80/20_300 h	0.35	0.79	58.48
PU_HPC 80/20_400 h	0.29	1.06	76.66
PU_HPC 80/20_500 h	0.28	1.03	68.75
PU_HPC 80/20_600 h	0.69	0.81	37.03

Thus, between 200 and 600 h of exposure to ageing conditions, the area corresponding to the free carbonyl groups (A_F) of PU increases (Fig. 6), mainly due to the hydrolytic process in the soft segment, leading to the formation of carboxylic acid fragments. The hydrolysis in the soft segments is masked by interconnected compact hard segments, also evidenced by the constant ordered area during the ageing process.³¹

The content of hard segments of PU also influences the degradation process in the blends

(Fig. 6). During the ageing process, an increase in the free carbonyl group, estimated as 67%, 83% and 77% for PU_HPC 20/80, PU_HPC 50/50 and PU_HPC 80/20, respectively, occurred after 500 h of exposure to simulated conditions.

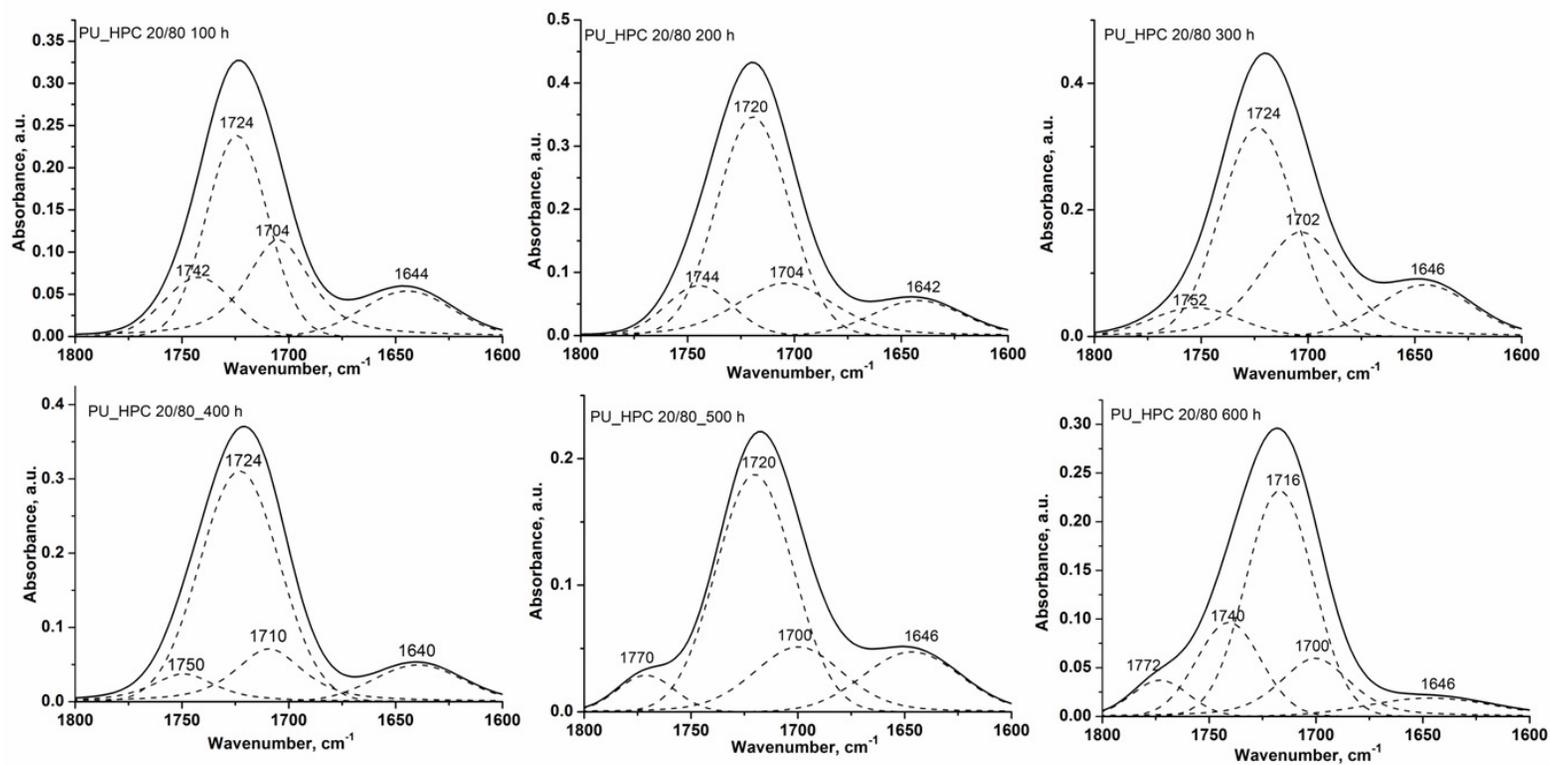


Figure 3: Deconvoluted IR spectra of the PU_HPC 20/80 blend in the 1600-1800 cm⁻¹ spectral region

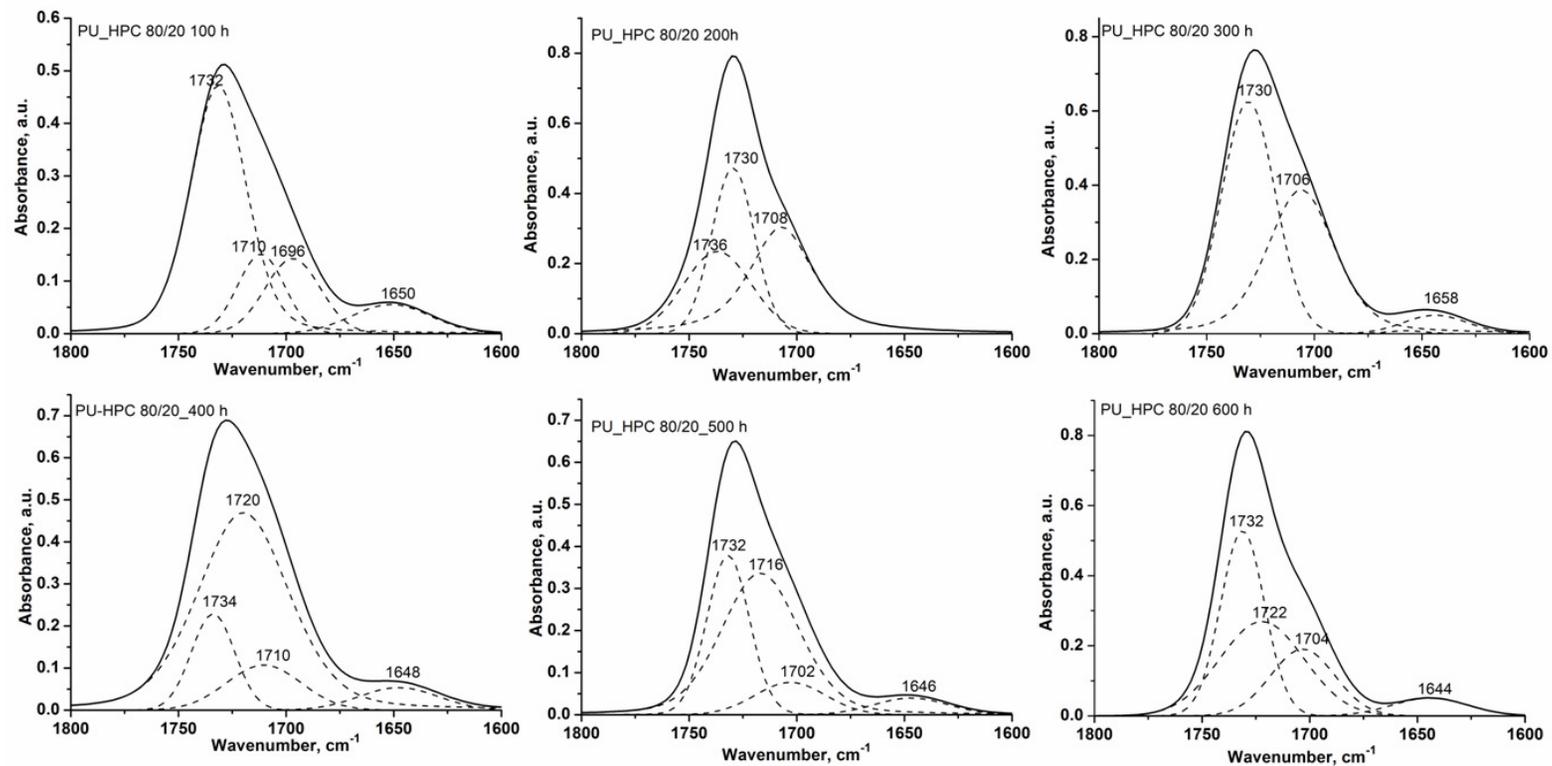


Figure 4: Deconvoluted IR spectra of the PU_HPC 80/20 blend in the 1600-1800 cm⁻¹ spectral region

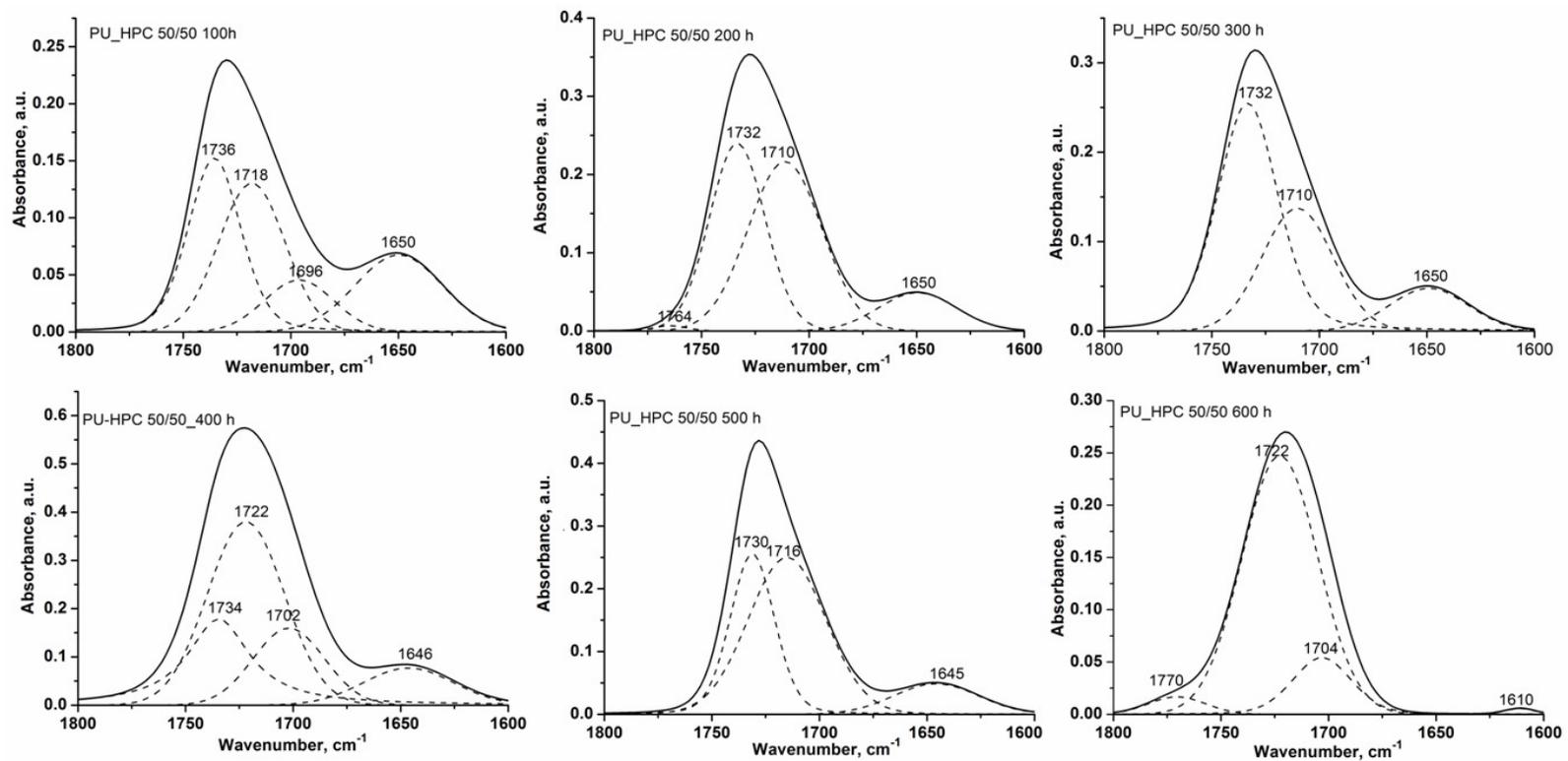


Figure 5: Deconvoluted IR spectra of the PU_HPC 50/50 blend in the 1600-1800 cm⁻¹ spectral region

Table 2
Curve-fitting results in the carbonyl spectral region of the HPC blends and starting polyurethane

Time of accelerated weathering	Sample	Free v/Area, %	C=O H-bonded	
			Disordered v/Area, %	Ordered v/Area, %
Initial	PU	1730/65.33	1702/25.79	1660/8.8
100 h		1730/30.09	1706/60.06	1644/9.84
200 h		1730/60.09	1710/32.02	1644/7.87
300 h		1730/45.94	1708/46.88	1646/7.17
400 h		1730/55.87	1710/38.09	1648/6.03
500 h		1732/35.33	1710/55.54	1650/9.12
600 h		1732/54.89	1708/38.89	1640/6.12
Initial	PU_HPC 20/80	1732/56.72	1710/19.33	1664/23.94
100 h		1724/50.29	1704/33.02	1644/16.68
200 h		1720/63.79	1704/23.5	1642/12.71
300 h		1724/50.98	1704/33.04	1646/15.98
400 h		1724/69.60	1710/18.04	1640/12.36
500 h		1720/59.95	1700/21.05	1646/18.99
600 h		1740/67.67	1700/22.06	1646/10.26
Initial	PU_HPC 50/50	1732/51.40	1710/19.38	1668/29.20
100 h		1718/48.83	1696/17.86	1650/33.30
200 h		1732/40.66	1710/47.93	1650/11.40
300 h		1732/56.22	1710/31.65	1650/12.11
400 h		1722/61.52	1702/23.88	1646/14.58
500 h		1730/33.63	1716/54.77	1646/11.58
600 h		1722/83.86	1704/15.45	-/-
Initial	PU_HPC 80/20	1730/60.69	1708/13.88	1670/25.42
100 h		1730/36.56	1710/40.83	1650/22.59
200 h		1730/25.71	1710/32.80	-/-
300 h		1730/52.27	1706/47.27	1658/5.38
400 h		1732/79.83	1710/13.19	1648/6.96
500 h		1732/77.72	1716/14.43	1646/7.84
600 h		1732/58.56	1704/31.52	1644/9.91

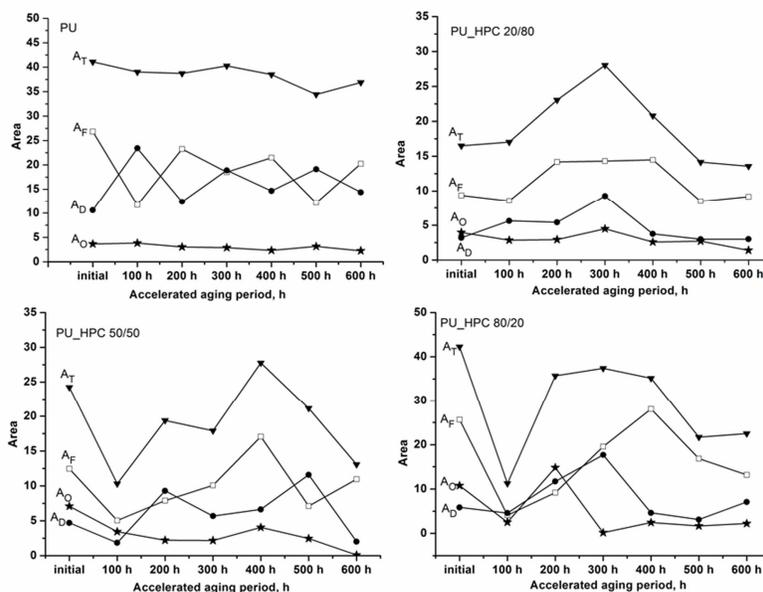


Figure 6: Plot of the areas for variations in the absorbance of “free” (A_F) and hydrogen bonded “ordered” (A_O) and “disordered” (A_D) carbonyl bands

A marked decrease of the whole area can be observed for PU_HPC 50/50 and PU_HPC 80/20 after 100 h of accelerated ageing, suggesting the dissociation of the hydrogen bonding network within the blends, followed by a structural reorganization of the polymeric chains during the degradation processes. In all the blends, a loss in the total area was observed after 600 h of exposure, suggesting mass loss in the hard segments of PU (Fig. 6).³²

CONCLUSION

Hydroxypropyl cellulose/polyurethane blends (PU_HPC 20/80, PU_HPC 50/50, PU_HPC 80/20) have been investigated under accelerated weathering conditions by FT-IR spectroscopy. FT-IR spectra confirm that all the blends are affected by combined UV irradiation, temperature and humidity exposure, causing significant degradation in the HPC component, while in the PU component, the hydrolytic effect is “masked” by the H-bonds within the hard segments. TCI, LOI and HBI (%) indexes have been evaluated, revealing non-uniform dependence on the ageing exposure time due to degradation and reorganization of the polymeric chains. The lowest values of TCI were obtained for PU_HPC 50/50 and PU_HPC 80/20, suggesting the impact of the HPC component on the stability of the blends. The LOI index was higher in the blends than in HPC, highlighting the impact of the PU component in the structural reorganization during the degradation processes. The main mechanisms of degradation were found to be hydrolysis and oxidation through hydroperoxide radicals, the IR spectra revealing the characteristic absorptions bands of the hydroperoxide species. The degradation process occurs in both components of the blends (HPC and PU), the total area in the carbonyl spectral region drastically decreases during long-term exposure. Polyurethane degradation mainly occurred by chain scission of polyesters, being also influenced by the HPC addition, the most stable blend being PU_HPC 20/80.

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