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Thermal Analysis of the Biodegradable Polymer PVA/PEO Blends

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Abstract: Poly(vinyl alcohol) (PVA) and poly(ethylene) oxide (PEO) are widely used water-soluble and biodegradable polymers that possesses high biocompatibility. In this work PVA/PEO blends were prepared via solution casting method, where the solvent was water. After drying, samples were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Since DSC could not confirm the possible intermolecular interaction between PVA and PEO, infrared spectroscopy with Fourier transform (FT-IR) was utilized. Finally, the TG analysis revealed that degradation of PVA/PEO blends proceeds through tree stages, similar as neat PVA. Contrary, neat PEO thermally degrade through only one stage showing better thermal stability in comparison to PVA.

Keywords: polyethylene oxide; polymer blends; polyvinyl alcohol; thermal analysis

1 INTRODUCTION

Poly(vinyl alcohol) (PVA) is a polar polymer with multi-hydroxyl groups which shows generally good mechanical and thermal properties. It also poses favourable biocompatibility and excellent barrier properties. Hence, PVA is an ideal material for tissue engineering applications, such as bone, cartilage, and the aortic heart valve [1]. Likewise, it can be synthesized from nonpetroleum raw material, which is important in the situation of petroleum scarcity. Thanks to its low cost, good film forming, high solubility in water, non-toxicity, easily process able, high dielectric permittivity and great insulating properties, PVA has been widely used in many different industries, like packaging, textiles, paints, building materials, electronic products, automotive, medicine, and other [2, 3]. On the other hand, poly (ethylene oxide) (PEO) is a semi-crystalline, water-soluble and biocompatible polymer of considerable industrial significance. It is utilized in organic–inorganic hybrid material in the field of functional coatings with superior barrier properties [1].

During the past few decades, numerous investigations have been carried out in order to develop blends of biodegradable polymers with good thermo-mechanical properties. The blending of two or more polymers is one possible approach for designing material with desired structural, thermal and mechanical properties. By this approach it is possible to tailor specific property to the requirement of applications, which cannot be achieved by one polymer alone. The investigations about electrical, optical, structural, thermal and degradation behaviour of the PVA/PEO systems have been performed [1-8]. However, most of authors focused on the interaction between PVA and poly(ethylene glycole) (PEG) [1, 6-8]. PEG refers to an oligomer and due to its molecular weight below 20,000, it has mostly been used as plasticizer in the PVA systems. Besides the obvious differences in molecular weight, PEG and PEO have similar physical properties, while contrary; their chemical properties are practically congruent.

Hence, the obvious aim of this investigation was threefold. Firstly, to prepare biodegradable polymer PVA/PEO blends via solution casting technique, in this case by using the PEO of higher molecular weight, which should result in compact biodegradable material, which can be, used as starting material for future investigations. The second aim was to evaluate structural properties and possible intermolecular interaction between PVA and PEO of higher molecular weight. Finally, the third aim of this work was to determine how PEO, as polymer of higher molecular weight, affected the thermal and degradation behaviour of the PVA in the blend and vice versa.

2 EXPERIMENTAL PART

2.1 Materials, Preparation and Methods

Materials used in this work were as follows: poly(vinyl alcohol) (PVA) 22,000 gmol^{-1}, BDH Prolabo, UK; poly(ethylene oxide) (PEO), 100,000 gmol^{-1}, Sigma-Aldrich, Inc., St. Louis, USA; deionized water.

Water-soluble polymers, PVA and PEO, were separately dissolved in deionized water and then mixed in different ratio (PVA/PEO = 100/0, 70/30, 50/50, 30/70 and 0/100). In order to completely dissolve and blend, the polymer blends were mixed at 400 rpm for two days at 40 °C. Next, each blend was poured into a Petri dish and dried two days at room temperature. The residual water was removed by drying obtained films in an oven for seven days at 40 °C.

Thermal characteristics of the PVA/PEO blend films were analysed via differential scanning calorimetry (Mettler Toledo DSC 823^{e}) in a nitrogen atmosphere (30 cm^{3}min^{-1}). Samples (15 mg) were heated (20 °C min^{-1}) from –90 to 280 °C, cooled at the same rate to –90 °C, and reheated to 280 °C. At –90 and 280 °C samples were isothermally for 5 minutes. The glass transition temperature (T_g) was determined from the second heating cycle according to international standard ISO 11357-2 [9] as the extrapolated onset temperature (T_{eig}), as midpoint temperature (T_{mg}), and as the extrapolated end temperature (T_{efg}). The corresponding change of the specific heat capacity (Δc_p) was determined as well. The melting and crystallization temperatures, as well as the enthalpies of melting and crystallization (ΔH_m and ΔH_c) were designated by ISO 11357-3 [10]. The melting/crystallization temperatures (T_m/T_c): the extrapolated onset temperature ($T_{eim/c}$), peak temperature ($T_{pm/c}$) and the extrapolated end temperature ($T_{efm/c}$). Detail info can be found in literature [11].

Thermogravimetric measurements of the PVA/PEO film samples were performed with PerkinElmer TGA 8000 in nitrogen atmosphere (40 $cm^3 min^{-1}$). Samples (5 mg) were heated (10 °C min^{-1}) in a temperature range 30-600 °C. To evaluate the thermal stability of the investigated polymers and their blends different criteria can be used. From TG and DTG curves the following characteristics were determined: the onset temperature (T_{onset}), the temperature at 5% mass loss ($T_{5\%}$), the temperature at the maximum degradation rate (T_{max}), the maximum degradation rate (R_{max}), the final mass (m_f) and the mass loss (Δm) for the corresponding degradation steps. Detail info can be found in literature [12].

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained with Perkin Elmer Spectrum Two FT-IR spectrometer via Universal Attenuated Total Reflectance (UATR) technique with diamond reflection crystal.

3 RESULTS AND DISCUSSION

3.1 Differential Scanning Calorimetry

Figs. 1-2 shows compared normalized DSC curves of the investigated PVA/PEO films, while the DSC parameters are tabulated in Tab.1; values in red for the PVA and in blue for PEO, respectively. The PVA is characterized by glass transition temperature at 74 °C (T_{mg}), with the endotherm of melting starting at 199 °C and exothermic peak of crystallization at 192 °C (T_{eic}). Likewise, the PEO curve is also characterized by one glass transition at –47 °C (T_{mg}), one melting endotherm at 59 °C (T_{eim}) and one exothermic peak at 43 °C (T_{eic}).

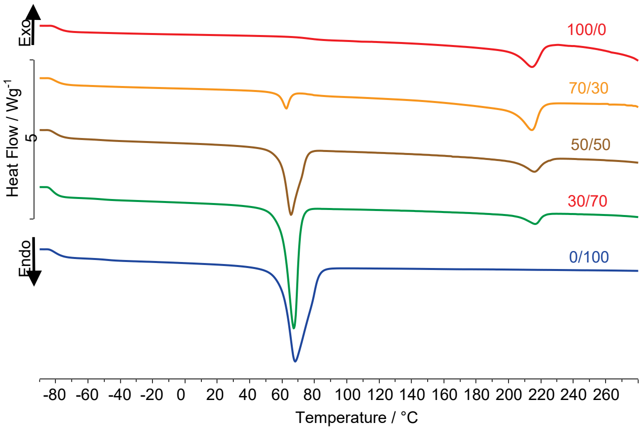

Figure 1 Comparison of the normalized DSC heating curves of the PVA/PEO blends

The DSC heating curves (second heating) of PVA/PEO blends show two endothermic peaks (Fig. 1), which is correlated to the melting of the PVA and PEO, respectively. The addition of PEO or PVA to the blends decreased values of the melting enthalpies of the PVA or PEO, respectively, but the shape of endothermic peaks remained almost identical as for neat polymers. The same trend is visible for the corresponding enthalpy of crystallization for the PVA and PEO, respectively, were also two exothermic peaks could be noticed (Fig. 2). However, upon addition of the PEO, the endothermic and exothermic curves of PVA shifted toward higher temperature in total by 4 (T_{eim}) and 3 °C (T_{eic}), respectively. On the other hand, by increasing PVA content, the melting temperature of the PEO decreased in total by 2 °C (T_{eim}), while the corresponding crystallization temperature increased in total by 2 °C (T_{eic}).

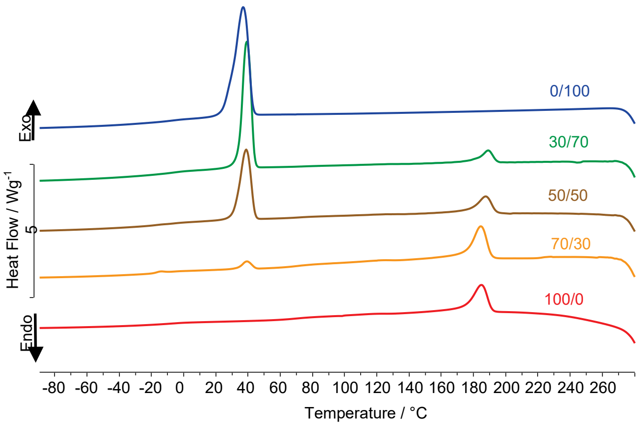

Figure 2 Comparison of the normalized DSC cooling curves of the PVA/PEO blends

The T_g transition of the PVA in the films is close to the melting endotherm of PEO, and therefore not detectable on DSC curves. Likewise, due to the high crystallinity of PEO, it is also difficult to observe the T_g of PEO. However, for sample with 50% of PVA content, the corresponding PEOs temperature increased toward T_g of PVA by 12 °C. Finally, the values of PEO's Δc_p decreased upon PVA addition, Tab. 1. It is evident that in the investigated PVA/PEO system possible interactions exist. Some clues could be found in the literature [1-8].

Table 1 DSC transition parameters of the PVA/PEO blends

Parameter		PVA/PEO				
		100/0	70/30	50/50	30/70	0/100
T_g (°C)	T_{eig}	67	-/-	-/–55	-/–57	–54
	T_{mg}	74	-/-	-/–35	-/–51	–47
	T_{efg}	83	-/-	-/–45	-/–46	–43
Δc_p (J g^{-1} °C^{-1})		0.31	-/-	-/0.10	-/0.13	0.14
T_m (°C)	T_{eim}	199	199/57	201/58	203/59	59
	T_{pm}	213	213/62	215/64	215/65	66
	T_{efm}	222	220/66	223/75	221/71	83
ΔH_m (J g^{-1})		45.6	55.9/8.5	24.7/65.6	12.8/98.5	134.2
T_c (°C)	T_{eic}	192	192/45	195/44	195/44	43
	T_{pc}	186	186/39	188/40	190/41	39
	T_{efc}	174	175/33	178/32	181/34	28
$-\Delta H_c$ (J g^{-1})		42.8	48.5/6.2	26.6/65.3	14.3/95.7	126.7

Ping et al. [1] investigated the porous PVA/PEG blend scaffold prepared through thermoplastic foaming using $scCO_2$ as the physical blowing agent. They used DSC to investigate the PEG effect on the thermal properties of PVA. According to the authors, with the addition of PEG, the melting peaks of PVA/PEG composites gradually shifted to a lower temperature, which they attributed to the hydrogen bonding of PVA-PEG. Likewise, authors concluded that PEG disturbed the molecular chain arrangement of PVA and interfered its crystallization.

In order to develop membranes, Gupta et al. [5] studied blends of PVA and PEO (300 000 gmol^{-1}) prepared by solution casting method (water) with different concentrations of carboxymethyl cellulose (CMC). Authors observed interactions in the investigated system and attributed them to the formation of hydrogen bonds. Although the DSC analysis showed decrease in crystallinity and the depression of melting temperature upon addition of CMC, latter authors did not investigate effect of PEO addition on the thermal properties of PVA, and vice versa. Falqi at al. [7] prepared PVA/PEG/graphene nanocomposites via solution casting technique. By utilizing DSC, they concluded that the T_m of PVA was not affected by PEG. However, upon addition of PEG, latter authors noticed a decrease in crystallinity, which was a result of the H-bonding between PEG and PVA. Likewise, they observed a decrease of T_g of the PVA/PEG blends, revealing PEG as plasticizer.

Summary, the noticed interaction between PVA and PEO(PEG) is evidently the product of hydrogen bond established between –OH from PVA and –O– from PEO. In order to confirm DSC results gained in this work, FT-IR analysis was used.

3.2 Fourier Transform Infrared Spectroscopy

The corresponding FT-IR spectra are presented on Fig. 3. PVA shows characteristic wide band of hydroxyl stretching assigned to the bonded hydroxyl in crystalline phase. As the PEO content increased in the blends, this band shifted to the higher wavenumbers (3271→3285 cm^{-1}). The particular characteristic of the PVA is formation of the hydrogen bonds (inter- and intra-molecular) between its OH groups, while in the PVA/PEO blends additional hydrogen bonds can be formed between the OH groups from PVA and PEO chains [1].

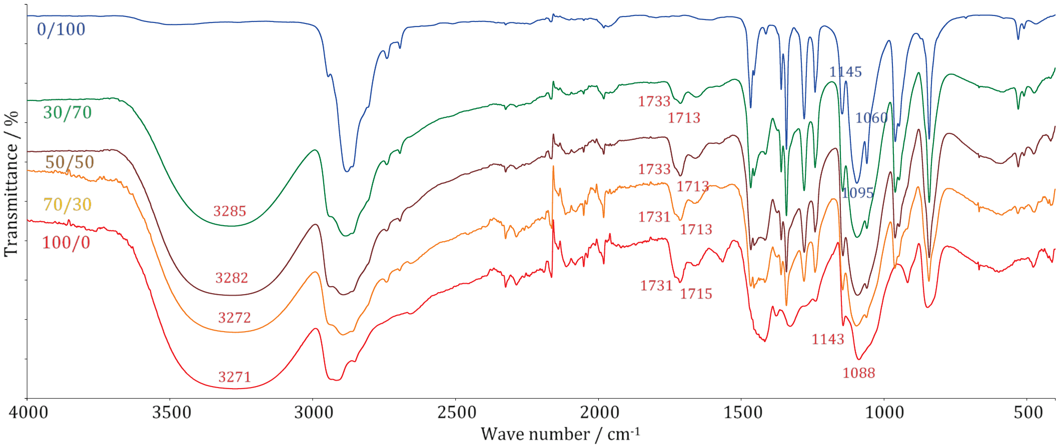

Figure 3 Comparison of the FT-IR spectra of the PVA/PEO blends

In addition, at higher PEO loadings above 50%, this band is preserved. Therefore, noticed slight shift of peak position and intensity of the –OH stretching vibration for all PVA/PEO blends, can be assigned to the hydrogen bonding [8]. The peaks between 1731 – 1715 cm^{-1} are due to the stretching of the C = O and C–O from acetate group remaining from partially hydrolyzed PVA [6, 13]. It is clearly visible that by increasing the content of the PEO, the intensity of the absorption bands decreased. Likewise, the band at 1731 cm^{-1} changes its shape from peak like to the shoulder like, while retaining its position. According to the Mansur et al. [13] the peak at 1143 cm^{-1} is related to the symmetric C–C stretching mode or stretching of the C–O where an intramolecular hydrogen bond is formed between two neighbouring OH groups. The intensity of this peak is influenced by the crystalline portion of the polymeric chains [13]. Increasing the PVA content in the blends, the peak position and intensity remained unchanged. This is in accordance with the result of the DSC analysis where the corresponding crystallization temperature of the PVA in the blends changed by only 2 °C in total (T_eic). In the range of 1000–1300 cm^{-1}, the crystalline phase of PEO is featured by the symmetrical stretching of the C-O-C group ("triplet") [14]. In the same spectral range, there is clearly visible peak at 1088 cm^{-1}, which can be assigned to the C-O-C stretching in the neat PVA [2]. Any alteration of intensity, shape or position of the "triplet" can be linked to the PEO-PVA interaction. However, the "triplet" isn't affected by PVA. Likewise, no change of the two peaks at 1145 and 1060 cm^{-1} is noted, and therefore PVA doesn't have impact on PEO crystallinity. This is in direct correlation with the conclusions made by DSC analysis, where it is evident that PVA did not affect crystallization process of the PEO in the blends.

3.3 Thermogravimetric Analysis

The Fig. 4 present TG and DTG curves of the investigated blends. Thermal degradation of PVA unfold through three degradation stages, Fig. 4(b), and begins at 78 °C (T_onset1) with a peak temperature at 105 °C (T_max1), representing the elimination of trapped water molecules. In the second stage at 265 °C (T_onset2) hydroxyl groups from PVA are eliminated. Finally, for the third stage at approximately 421 °C (T_onset3) a conjugated structure is formed from the product of the second stage of degradation [15, 16]. On the other hand, PEO decomposes by only a single degradation stage, beginning at 379 °C (T_onset) with T_max at 401 °C. It is evident that PEO, in comparison to PVA, is thermally more stable. PEO degradation proceeds by the random chain scission of C-O bonds [17] with the total weight loss of 95.4%. Although thermal degradation of the PEO proceeds through one stage, according to temperature range (*) its characteristics belong to the third degradation stage; Tab. 2. However, thermal degradation of all PVA/PEO blends, as well as PVA, proceeds through three stages (Fig. 4). The first two stages can be associated to the PVA, while the last one match the PEO degradation temperature domain.

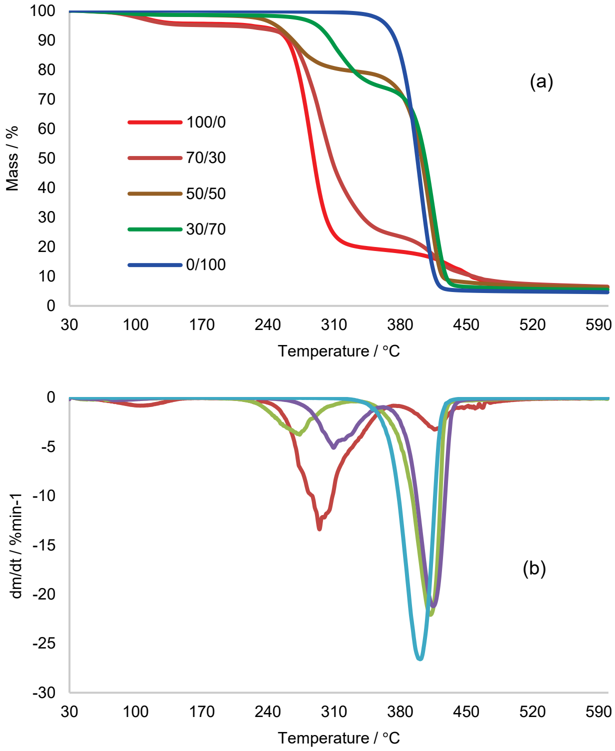

Figure 4 Comparison of the TG (a) and DTG (b) curves of the thermal degradation of the PVA/PEO blends

Table 2 Thermal degradation parameters of PVA/PEO blends

PVA/PEO	T_{onset} / °C	T_{max} / °C	R_{max} / %min^{-1}	Δm / %	m_f / %
1° degradation stage					
100/0	78	105	0.9	4,4	95,6
70/30	72	104	0.8	0,6	95,1
50/50	41	69	0.2	1,4	98,6
30/70	52	77	0.3	1,4	98,6
0/100	-	-	-	-	-
2° degradation stage					
100/0	265	289	20,7	76,7	18,9
70/30	269	295	13,4	71,2	23,9
50/50	241	274	3,8	19,1	79,5
30/70	288	310	5,1	24,5	74,1
0/100	-	-	-	-	-
3° degradation stage					
100/0	421	455	2,4	12,5	6,4
70/30	400	416	16,8	17,4	6,5
50/50	389	412	22,1	73,3	6,2
30/70	396	415	21,2	68,6	5,5
0/100*	379	401	26,6	95,4	4,6

In the first stage, PVA/PEO blends start thermally degrading at lower temperatures in comparison to PVA. However, in the second stage, the trend is miscellaneous and the blend composed of the 50% of PVA and 50% of PEO showed the lowest thermal stability characteristics. On the other hand, blend with 70% of PEO exhibited the highest values, confirming PEOs stabilizing effect on PVA.

Similarly, Ghalia and Dahman [8] attributed higher thermal stability to the sufficient cross-linkage and interaction between PVA and PEG. Likewise, this shifting in the second stage to the higher degradation temperatures for the blend 70/30, Hameed [18] attributed to the good compatibility of PVA and PEO, resulting in improved thermal stability of polymer blends. Finally, in the third stage, alteration of values of T_{onset} and T_{max} for all blends are minor and practically negligible.

4 CONCLUSIONS

In this work biodegradable polymer PVA/PEO blends were prepared via solution casting technique. The main scope was to estimate thermal and degradation behaviour of the investigated blends, as well as possible intermolecular interaction between PVA and PEO. The minor extenuation of melting and crystallization temperatures at increased PEO content (70%) indicated the existence of mild interaction between PVA and PEO as a product of hydrogen bonding. Likewise, the slight shift of the –OH stretching vibration for all PVA/PEO blends, confirmed hydrogen bonding formation between PVA and PEO. Thermogravimetric analysis revealed that PEO is more thermally stabile than PVA. Hence, shifting of the characteristic degradation temperatures in the second stage to the higher values for the blend with 70% of PEO is the result of the good compatibility of PVA and PEO, which resulted in improved thermal stability of polymer blends. Finally, this investigation presents a valuable input for the future research in which another method of blend preparation should be considered, and consequently the application of such gained blends propounded.

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