

Copolymers based on poly(vinyl alcohol) and acrylamide

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Recently, there was investigated the modification of hydrophilic polymers by graft copolymerization techniques to prepare products with good biocompatibility and biodegradability for hydrogels or highly water absorbent polymers. Poly(vinyl alcohol) (PVA) a highly hydrophilic polymer can be modified with vinyl monomers to obtain copolymers with improved properties. The study presents the synthesis of poly(vinyl alcohol)-acrylamide copolymers using as radical initiator benzoyl peroxide or as redox initiator potassium persulfate/ferrous sulfate, by solution polymerization procedure in water or ethylene glycol/water (1/3) mixture. The gravimetric ratio PAV/acrylamide was variable: 1/1; 1/2.33; 2.33/1. The obtained copolymers were characterized by infrared spectroscopy, elemental and thermal analyses, and swelling behaviour in distilled water.

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1. Introduction

Graft copolymers have been widely used for compatibilization of immiscible polymer blends as well as the improvement of interfacial adhesion in composites. Poly(vinyl alcohol) with varying physical properties can be obtained from poly(vinyl acetate) by varying the solvent and temperature used in the vinyl acetate polymerization [1]. It has been widely utilized in polymer modifications as it is readily available, it is inexpensive and it has hydroxyl groups present. Graft copolymers from poly(vinyl alcohol) have been prepared especially by irradiation techniques. PVA with grafted methyl methacrylate has been studied as membrane for hemodialysis [2]. Graft copolymers consisting of 50 % PVA, 25 % poly(vinyl acetate) and 25% grafted ethylene oxide units have been used to prepare capsules for drugs which do not require any additional plasticizers [3]. Crosslinked PVA derivatives have been reported by reacting their hydroxylic groups with dianhydrides and diisocyanates [4]. Grafting a functional oligomer chain into water soluble biodegradable polymers, such as PVA, is a potential route to obtain biodegradable functional polymers.

The aim of the research focuses on grafting PVA with acrylamide, to obtain copolymers with improved properties, biodegradable and biocompatible, that will be further used as hydrogels or water absorbing copolymers.

2. Experimental

2.1. Materials

The raw materials used in our experiments are available as commercial products. Poly(vinyl alcohol), acrylamide, benzoyl peroxide, potassium persulfate, ferrous sulfate, ethylene glycol were used without further purification.

2.2. Synthesis of copolymers

The synthesis of copolymers was done in aqueous solution and in ethylene glycol/water mixture (1/3). To determine the synthesis conditions, different gravimetric ratio PVA/acrylamide (Table 1) and benzoyl peroxide or redox system (potassium persulfate/ferrous sulfate) as initiators were used.

PVA was dissolved in water or ethylene glycol/water mixture at 60-70 °C, solutions 10 wt % were obtained, then the adequate quantity of acrylamide and initiator (0.4 wt % to comonomers) were introduced under continuous stirring in the reaction vessel. Further, the temperature was raised and maintained at 85-90 °C for 5 hours. The obtained products were precipitated in methanol, filtered and vacuum dried at 60 °C.

Table 1. Synthesis conditions of copolymers.

Sample	Gravimetric ratio PVA/AAm	Solvent	Initiator	Temperature (°C)	Time (h)
1	1/1	H ₂ O	POB	90	5
2			Redox	75-80	
3		EG/ H ₂ O	POB	90	
4			Redox	75-80	
5	2,33/1	EG/ H ₂ O	POB	90	
6			Redox	75-80	
7		H ₂ O	Redox	75-80	
8			POB	90	
9	1/2,33	EG/ H ₂ O	POB	90	
10			Redox	75-80	
11		H ₂ O	POB	90	
12			Redox	75-80	
PAAm	Acrylamide	EG/ H ₂ O	Redox	80-85	6

2.3. Methods of investigation

IR spectra of the crosslinked copolymers were recorded on spectrophotometer M80 type using KBr pellets for sample preparation.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) were recorded on a derivatograph Q-1500 D tip MOM-Budapest (Hungary), under the following operational conditions: sample weight 50 mg, heating rate 10 °C/min, in air flow of 30 mL/min and reference material α -Al₂O₃.

The DSC thermal analyses were carried out by means of a Mettler 12E type differential scanning calorimeter (Switzerland) with a heating rate of 10 °C/min in nitrogen atmosphere. The first heating run was carried out with a 10-12 mg sample in the temperature range between room temperature and 300 °C. The second heating run was performed with samples which were suddenly cooled to room temperature. Pure indium was used as a standard for calorimetric calibration.

The swelling degree of the synthesized copolymers in distilled water, was studied at 25 °C.

3. Results and discussion

Grafting reaction of PVA with acrylamide was carried out in aqueous medium, as well as in EG/water mixture (1/3), using benzoyl peroxide or potassium persulfate/ferrous sulphate as initiators.

The obtained copolymers were characterized by IR spectroscopy, thermal analyses (DSC, DTG) elemental analyses and water swelling degree.

In Figs. 1 and 2, IR spectra of PVA-grafted with acrylamide, unmodified PVA and acrylamide, are presented. The specific absorption bands at 1650 cm⁻¹ corresponding to ν C=O group (amide band 1) and 1600 cm⁻¹, corresponding to δ NH group (amide band 2) are found in the synthesized copolymers too, demonstrating that PVA grafting reaction took place.

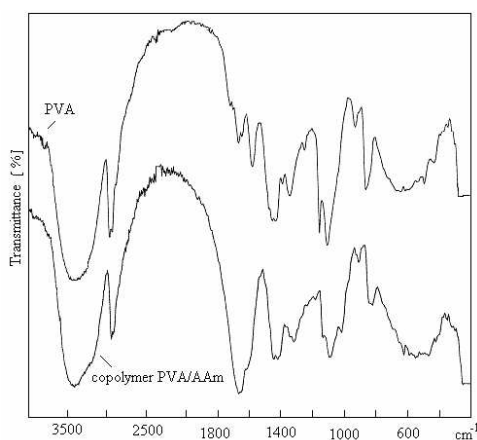


Fig. 1. IR spectra of grafted copolymer PVA/acrylamide and PVA.

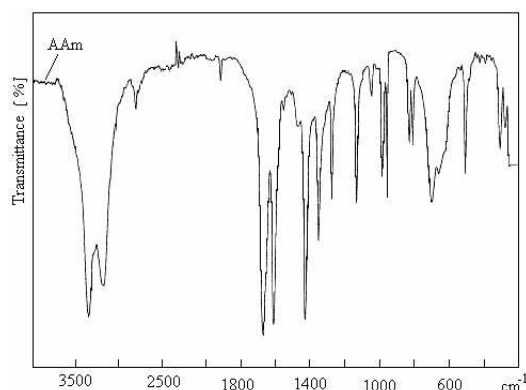


Fig. 2. IR spectra of acrylamide.

The elemental analysis of the synthesized copolymers shows that nitrogen exists in the copolymer structure, varies between (3.50-10.42 wt %), depending on the initial ratio of the components in the grafting reaction (Table 2).

Table 2. Elemental analysis of PAV/acrylamide copolymers.

Sample	C %	N %	H %
1	63.02	5.94	10.10
3	51.17	8.59	5.95
7	54.79	3.94	9.36
8	54.21	3.50	8.11
9	53.05	8.79	5.94
11	59.67	10.42	5.99
Polyacrylamide	42.77	12.63	6.29

In Fig. 3 are presented the TG curves referring to the weight losses determined by oxidative thermal decomposition of the main synthesized copolymers, and in Table 3 characteristics concerning the thermal stability. The copolymers present weight losses of 50 % at a raised temperature than of PVA, consequently they have a better thermal stability.

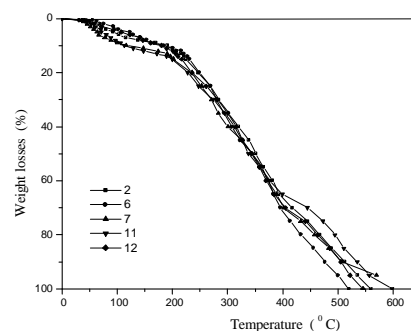


Fig. 3. TG diagrams of synthesized copolymers.

Table 3. Thermogravimetric data.

Sample	T ₁₀ °C	T ₅₀ °C	T _i °C	T _f °C	W _{Ti-Tf} %	Ea KJ/mol	n
2	192	351	165.5	436.5	64.5	50.82	1.4
6	185	344	198.5	427.5	70	68.50	1.7
7	117	344	153.5	424	61.8	48.54	1.3
11	113	338	168.5	427.5	55.9	66.21	1.9
12	181	344	172	427.5	62.4	53.72	1.3
APV	225	270	153	340	55	95	1.2

T₁₀, T₅₀ temperature corresponding to 10 % and 50 % weight loss. T_i, T_f, the initial and ultimate temperature of the domain on which Ea and n were calculated

The activation energy as a function of the conversion of the thermal decomposition reaction (Fig. 4), presents a quick lowering until a conversion of 0.10 wt %, then its variation is almost linear. The sudden lowering of Ea observed on the first part of the interval, suggests that at the beginning the decomposition reaction has an autocatalytic behaviour, due to oxygen traces in the copolymers that act as catalysts of the thermal decomposition processes.

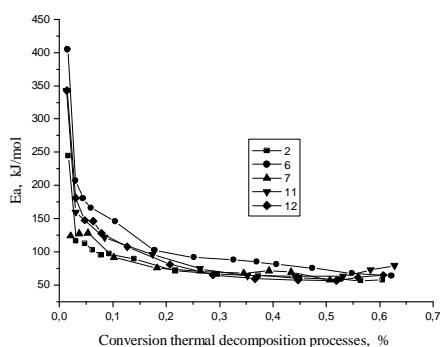


Fig. 4. Dependence of Ea on conversion degree of thermal decomposition processes.

In Fig. 5 and Table 4 are presented the thermal characteristics determined by differential scanning calorimetry. The glass transition temperatures (T_g) of the copolymers are lower than of PVA, and melting temperatures (T_m) and melting enthalpy (ΔH) have more raised values.

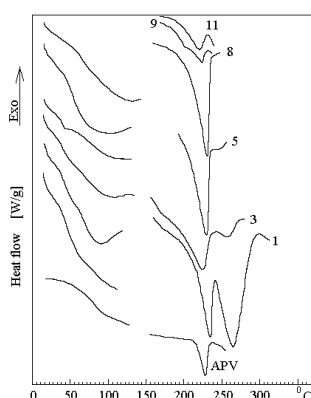


Fig. 5. DSC curves of synthesized copolymers.

Table 4. DSC characteristics.

Sample	T _g °C	T _m °C	ΔH J/g
1	47	230	43.60
3	45	218	67.80
5	45	225	47.48
8	40	228	82.55
9	52	220	33.63
11	58	220	15.80
APV	70	210	22.61

The swelling ratio and equilibrium water content for the synthesized copolymers are presented in Figs. 6 and 7. The samples 6 and 12 present swelling ratio of 1.3 g water/g dried copolymer, and equilibrium water content about 70-71 % after 2-3 hours immersion in distilled water at 25 °C. In the case of copolymers 3 and 5, the swelling ratio doesn't exceed 0.4, and the equilibrium water content 30 wt %, while for the copolymers 1 and 11 these values attain 0.7 and 65 % respectively in 1h. The lower values of these parameters are due also to the fact that after water immersion and swelling, the copolymers are divided into fragments; they are partially dissolved and their weight lowers, thus weighing errors at determining swelling behaviour are noticed. From the data presented we can notice that in the case of redox initiated copolymers, the swelling characteristics are better. To prevent the division of the synthesized copolymers into fragments, their crosslinking with adequate crosslinking agents is required.

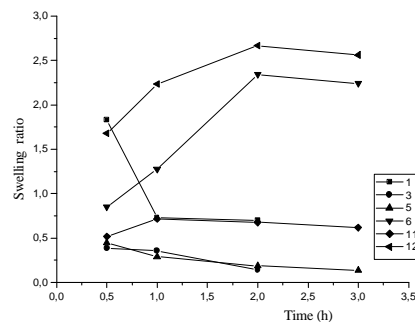


Fig. 6. Swelling ratio in distilled water of synthesized copolymers at 25 °C.

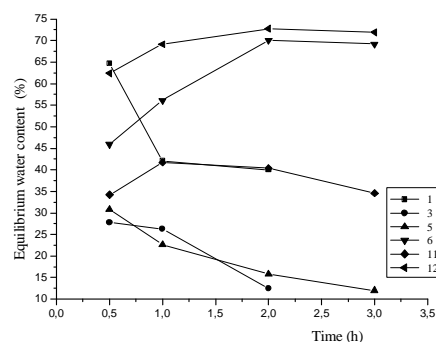


Fig. 7. Equilibrium water content of synthesized copolymers at 25 °C.

4. Conclusion

Copolymers based on PVA-acrylamide have been obtained. The IR spectra and elemental analyses demonstrate that acrylamide has been grafted on PVA. DSC and DTG analyses prove that the copolymers have a better thermal stability than unmodified PVA. The swelling behaviour demonstrated that copolymers must be crosslinked and we intend to synthesize hydrogels using usual PVA crosslinking agents.

References

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