



*Dedicated to the memory of
Professor Victor-Emanuel Sahini (1927–2017)*

THERMAL STABILITY OF BIO-NANOCOMPOSITE FILMS BASED ON POLY(VINYL ALCOHOL)/STARCH/CELLULOSE NANO-CRYSTALS

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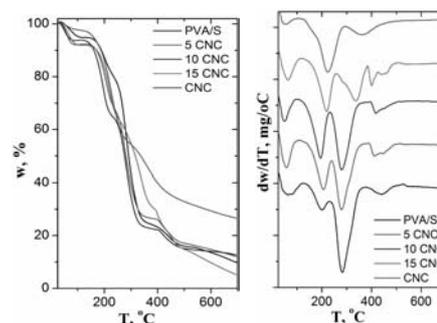
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Thermal stability of polymeric materials is one of the most important properties which ultimately govern the mechanical properties, durability, spectral stability, shelf lives, and life cycles of polymers. In this context, TGA is a useful method to investigate the thermal stability of polymeric systems.

The aim of this work is to evaluate the influence of starch (S) and cellulose nano-crystals (CNC) content on the thermal stability of poly(vinyl alcohol)(PVA)/starch (S) and PVA/S/CNC films. The TGA curves of the studied materials, registered in the 25-700 °C temperature range, show that all samples exhibited four distinct and well-separated weight-loss processes which are better evidenced in derivative thermogravimetric (DTG) curves. The shifting to higher value of both onset and maximum temperatures and the decreasing of the mass loss for the blends containing CNC suggests the formation of more compact structures, confirming the reinforcing effect of the CNC.



INTRODUCTION

The large utilization of petroleum based polymers (such as polystyrene, polyethylene, etc.) in packaging industry has caused serious pollution problems. Therefore, an alternative for the traditionally used non-biodegradable petroleum based polymers is the use of environmentally friendly natural polymers such as cellulose, starch, chitin, etc. that are biodegradable and renewable.¹ However, their properties being weaker as compared to those of the synthetic ones, the incorporation of nanosized reinforcements into the biopolymer-based materials can enhance their commercial potential. For that, different nanofillers

can be added, and recently a high attention was given to the naturally derived organic ones due to their biodegradability, renewability, nontoxicity and biocompatibility.²

Poly(vinyl alcohol) (PVA), an important polymer in packaging industry, is suitable to be used due to its ecofriendly properties. Moreover, PVA is a water-soluble, biodegradable synthetic polymer, it is biocompatible, chemically resistant, and presents excellent physical and gas barrier properties. It can be also used in combination with starch and numerous studies on PVA/starch have been reported.³⁻⁵ In PVA/starch blends, strong hydrogen bonds between starch and PVA and a network structure were observed.

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Due to its large availability and relatively low price, starch is one of the most promising polysaccharides for biodegradable films. Films made from starch have some remarkable properties – they are isotropic, odorless, colorless, non-toxic and biologically degradable. On the other hand, starch has some disadvantages which limit its use. Compared to conventional films, starch has a strong hydrophilic character and poor mechanical properties, which make it inadequate for some packaging purposes.^{6,7}

To improve the properties of the PVA/S blends, different fillers are usually used and one which received more attention in recent days is cellulose nanocrystals. Due to their higher crystallinity and good mechanical properties combined with a higher surface area and active interfaces, cellulose fibers modified at nanometer size induce seriously improved mechanical properties to polymer matrices as compared to common cellulose fibers.⁸ Thus, cellulose nanocrystals (CNCs) are used as nanosized reinforcement in polymers due to properties such as a large specific surface area, high modulus of elasticity and ability to act as a significant reinforcement at low filler loading levels. Other advantages are the biocompatibility and biodegradability, their nonabrasive nature and nontoxic character.

The thermal resistance is a significant property of the polymer composites – it governs most properties such as the durability, spectral stability, shelf lives and life cycles of the polymers, the mechanical properties. Once degradation begins, the above properties will gradually deteriorate.² The thermogravimetric (TG) measurements offer basic and important information about the composition and the thermal properties of the materials. In TG measurements, the weight loss of a sample is measured as a function of temperature or heating time, accompanied by emitting volatile gases from the sample. Due to its inherent measurement principle, qualitative information is hardly obtained by TG, but the measurement offers quantitative information on the weight loss of a sample.⁹

The aim of this study was to evaluate the effect of the incorporation of nanocellulose in the PVA/starch composites.

MATERIALS AND METHOD

Materials

All chemicals - polyvinyl alcohol (PVA, with a $M_w=146000-186000$, 99+% hydrolysed), starch (S, from potatoes), glycerol (>99.5%) and

sulphuric acid were supplied from Sigma Aldrich. Cellulose nanocrystals (CNC) were obtained by acid hydrolysis from cotton wool.

Blends preparation

To obtain the PVA/S blends, solutions of 3% of PVA and starch were obtained by solubilization of the particles in distilled water, at 90°C and 1200 rpm for 3 h and 1 h, respectively. After complete dissolution of the components, 20 mL of solutions (to obtain 90 PVA/10 S, 75 PVA/25 S and 50 PVA/50 S polymeric blends) were mixed with 0.1 mL of glycerol. For PVA/S/CNC films, 5, 10 and 15% CNC in suspension, respectively were added to the 95, 90, and 85% of each of the previously obtained solutions. To ensure a homogenous solution, all blends were stirred for a period of 30 min at 90 °C and 1000 rpm. The solutions were then cast into glass petri-dishes and dried in an oven for a period of 24h at 45 °C.

Method

Thermogravimetric analysis (TGA) was carried out under constant nitrogen flow (200 mL/min) at a heating rate of 10 °C/min using a Mettler Toledo TGA/SDTA 851 balance. The heating scans were performed on 3–5 mg of sample in the 25–700 °C temperature range. The kinetic parameters have been evaluated by integral and differential methods. The kinetic parameters have been evaluated by the integral Coats-Redfern method using VERSATILE program.

RESULTS AND DISCUSSION

The thermal stability of a polymeric material depends on the inherent characteristics of the samples, as well as on the molecular interactions between the different macromolecules. The chain cleavage or the bond dissociation of the macromolecules takes place when the supplied thermal energy exceeds the bond dissociation energy of the respective chemical bonds.

The TGA curves in the 25-700 °C temperature interval of the studied materials are shown in Fig. 1a and 1c. The first-order derivatives of TGA curves (DTG) (Fig. 1b and 1d) reveal the temperature for the maximum decomposition rate. The curves show that all samples exhibit four distinct and well-separated weight-loss processes,

better evidenced in derivative thermogravimetric (DTG) curves. For all studied samples, the first process occurs in the temperature interval between 25 and 112-127 °C with a maximum between 51 and 66 °C and a corresponding mass loss of 5-8 wt% (Table 1). This process is related to the removal of the physically adsorbed water. The second thermogravimetric process takes place between 112-127 and 220-250 °C with a temperature for the maximum decomposition rate at about 196-220 °C. Low molecular weight volatile compounds like CO₂, CH₄, and/or primary alcohols can be eliminated during this stage from the polymeric structures, especially from the side chains and end chains groups.¹⁰⁻¹² In the case of PVA/S films, some differences between decomposition temperatures as compared to pure PVA and starch samples were observed. The temperature corresponding to the maximum decomposition rate of this process is shifted at higher values, from 112 °C in the case of PVA and 122 °C in the case of starch, to 127 °C for blends. With increasing the starch content in the blends, the temperatures corresponding to the end of this stage and to the maximum decomposition rate are higher. Also, as in the case of pure components, this stage is characterized by volatiles release. The shifting at higher temperatures is determined by the physical interactions of the blending components.⁵

The main decomposition process of PVA is in the 220-357 °C temperature range, with a maximum at 266 °C. This stage is due to the decomposition of PVA main chain and involves dehydration of the hydroxyl groups and/or the formation of volatile organic compounds which subsequently produce conjugated unsaturated structures like acetaldehyde, benzaldehyde, acrolein, and the decomposition of polyene macroradicals to cis and trans derivatives.^{10,13} The formation of these volatile organic compounds may be due to the scission of the carbon-carbon bonds, leading to the generation of carbonyl end functional groups products.⁵ The percentage of mass loss in this step is about 47%.

On the other hand, in the case of starch this decomposition process starts at 244 °C and ends at 333 °C. The temperature for the maximum decomposition rate is at 290 °C and the mass loss is about 40 wt%. This step involves elimination of the polyhydroxyl groups accompanied by depolymerization and decomposition. Dehydration of neighbouring hydroxyl groups in the glucose ring may also occur, resulting in the formation of

C=C bonds or breakdown of the glucose ring. The primary attack is the hydrolysis of α -1,4 glucosidic linkages in the amylose and amylopectin molecules. In addition, the scission of α -1,6 linkages may occur, and α -1,4 linkages are more susceptible to hydrolysis than α -1,6 linkages.¹⁴ At the same time, aldehyde groups may result as end groups, when the glucose ring is fractured. Increasing the temperature may generate aromatic rings, such as substituted benzene and furan structures with either -CH₂- or -CH₂-O-CH₂- as the main linkages between the aromatic groups.¹⁵

In the case of PVA/S blends the temperatures for the maximum decomposition rate in this stage are shifted at higher values as compared to pure PVA films. Thus, for the sample containing 90% PVA/10% S this maximum is shifted at 281 °C, for the sample containing 75% PVA/25% S at 320 °C and in case of the sample containing 50% PVA/50% S at 303 °C with a shoulder at 340 °C. This indicates an increase in the thermal stability of the polymeric blends and can be due to the crosslinking between the PVA, S and glycerol.

The last decomposition process of PVA is observed in the 384-518 °C thermal region, with a maximum at 420 °C and a shoulder at 442 °C. The mass loss is of 13.3 % and is due to thermal decomposition of primary polyenes to cis and trans derivatives followed by their cyclization and the condensation of polyaromatic structures.^{3,13} At about 520 °C the decomposition of the PVA sample is finalized, no more mass loss taking place for further increasing the temperature. The residual percentage of the weight was equal to 15.9 % at 700°C.

Starch presents a last decomposition process in the temperature range between 300 and 464 °C, with a temperature for the maximum decomposition rate at 348 °C, and a mass loss of about 11.5 wt %. The decomposition process finalizes at 464 °C, and the remained residual mass at 700 represents 26.8 wt %.

As for the blends, both onset and maximum decomposition temperatures for this stage are shifted to higher values (as for the previous process). Thus, for the blend containing 10 % S, the temperature for the maximum decomposition rate is at 442 °C, with a mass loss of 8.8 wt%; for the blend containing 25% S the temperature for the maximum decomposition rate is at 501 °C with the mass loss of 6.1 wt%; and in the case of the blend containing 50% S the temperature for the maximum decomposition rate is at 486 °C, with the mass loss of 9.8 wt%. The residual mass for the blends at 700 °C is of 15.6 wt%, 12.3 wt% and 16.3 wt%, respectively.

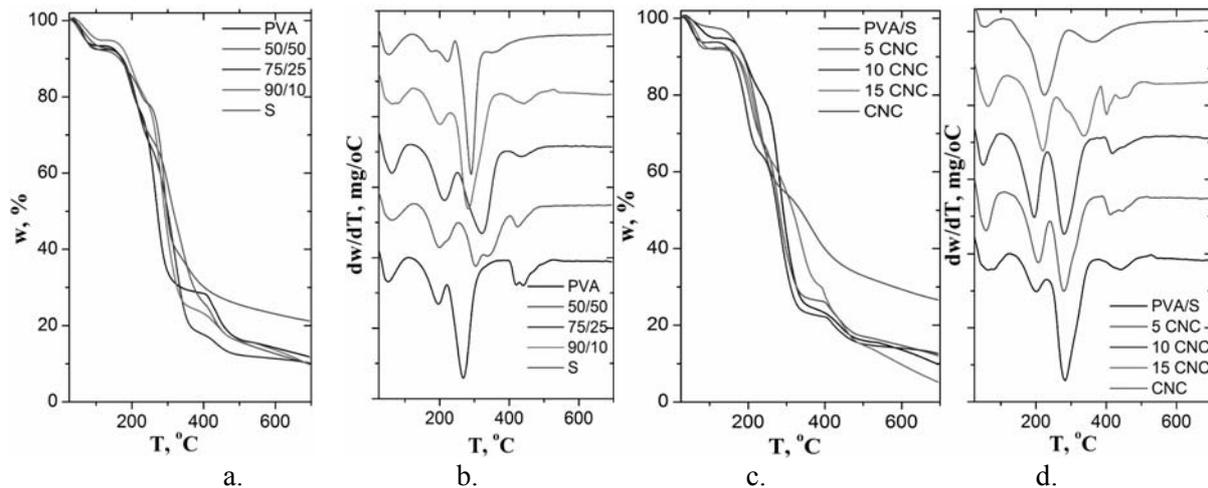


Fig. 1 – TG/DTG curves of PVA/S (a, b) and PVA/S/CNC blends (c, d).

Table 1

TG/DTG results for PVA, S and PVA/S blends

T	PVA	90% PVA/10% S	75% PVA/25% S	50% PVA/50% S	S
T _{i1} , °C	25	25	25	25	25
T _{m1} , °C	51	66	63	63	54
T _{f1} , °C	112	127	108	127	122
Δw ₁ , wt%	6.6	5.1	7.6	7.2	7.9
T _{i2} , °C	112	127	127	127	122
T _{m2} , °C	196	200	213	198	222 (T _{sh} 176)
T _{f2} , °C	220	233	252	254	244
Δw ₂ , wt%	16.6	14.5	25.1	23.6	13.9
T _{i3} , °C	220	233	252	254	244
T _{m3} , °C	266	281	320	303 (T _{sh} 340)	291
T _{f3} , °C	357	372	384	400	333
Δw ₃ , wt%	47.4	56.0	48.9	43.1	40.0
T _{i4} , °C	384	372	398	400	333
T _{m4} , °C	420 (T _{sh} 442)	442	433	424	348
T _{f4} , °C	518	528	501	486	464
Δw ₄ , wt%	13.3	8.8	6.1	9.8	11.5
Δw _{res} , wt%	15.9	15.6	12.3	16.3	26.8

Inclusion of cellulosic reinforcement is usually known to reduce the thermal stability of the composites with commodity thermoplastic matrices (polyethylene, polypropylene, etc.).

From Figs. 1c and 1d and Table 2, only three decomposition stages are evidenced for pure CNC, whereas for the PVA/S/CNC films four steps of the decomposition processes can be observed. During temperature increase from room temperature to 120 °C a 2 to 8 wt% decrease in the weight of the samples takes place. This process corresponds to vaporization of moisture from the samples.

The second step of mass loss of cellulose observed between 115 and 290 °C is followed by the third one in the 300–493 °C range. The temperatures corresponding to the maximum decomposition rates were found at 222 °C and 361 °C, with a mass loss of 42.6 wt% and 22 wt%,

respectively. The decomposition process finalizes at about 500 °C, and the remained residual mass at 700 is of 33.3 wt%. At temperatures below 300 °C, the degradation of glycosyl units of cellulose is accompanied by the evolution of water, carbon dioxide and carbon monoxide. In contrast to the relatively slow degradation of cellulose at lower temperatures, above 300 °C a rapid depolymerization of cellulose molecules proceeds, largely by cleavage of glycosyl units leading to the formation of 1,6-anhydro-β-D-glucopyranose (levoglucosan). At higher temperature direct fission of cellulose and the levoglucosan exposed to intense heat results in breakdown of the molecule to a variety of low molecular weight products, including carbon dioxide, carbon monoxide, water, hydrocarbons (acetaldehyde, glyoxal and acrolein) and hydrogen.^{16,17}

Table 2

TG/DTG curves of 90% PVA/10% S blends with different amounts of CNC

T	0 % CNC	5% CNC	10 % CNC	15% CNC	CNC
T _{i1} , °C	25	25	25	25	25
T _{m1} , °C	62	57	51	64	52
T _{f1} , °C	125	110	96	118	95
Δw ₁ , wt%	5.2	7.8	6.3	8.1	2.2
T _{i2} , °C	125	110	103	118	115
T _{m2} , °C	202	207	194	219	222
T _{f2}	232	239	232	259	290
Δw ₂ , wt%	14.3	24.5	28.9	28.9	42.6
T _{i3}	232	239	232	259 (T _{sh} 287)	300
T _{m3}	282	279	278	336	361
T _{f3}	376	379	371	384	
Δw ₃ , wt%	56.3	41.2	42.0	32.5	
T _{i4}	376	379	393	384	
T _{m4}	441	410 (T _{sh} 449)	415	401, 446	
T _{f4}	528	518	527	491	493
Δw ₄ , wt%	8.6	9.8	8.0	15.3	22.0
Δw _{res} , wt%	15.6	16.7	14.7	15.3	33.3

For the blends containing CNC, the second decomposition stage presents a temperature for the maximum decomposition rate at 207 °C and a mass loss of 25 wt% (for the blend containing 5% CNC), at 195 °C and a mass loss of 29 wt% (for the blend containing 10 % CNC) and at 219 °C with a mass loss of 29 wt% (in case of the blend containing 15% CNC), respectively. The increase of the mass loss arises from the decomposition of glycerol and small amounts of PVA/S blends and also due to the decomposition of cellulose with the formation of small molecules like CO₂, small aliphatic compounds or primary alcohols.

The third decomposition process takes place at higher temperatures as compared to the blends without CNC, at about 279 °C, 278 °C and 336 °C. The shifting to higher values of both onset and maximum temperatures and the decreasing of the mass loss, in the case of blends containing CNC, suggests the formation of more compact structures and confirms the reinforcing effect of CNC.

The last decomposition process is situated in the 376-520 °C temperature interval for all studied samples. In this case, the value corresponding to the maximum decomposition rate appears between 415 and 446 °C, with a mass loss between 8 and 15 wt%. A small increase of the mass loss is evidenced in case of the samples containing 15% CNC, whereas for the blends containing 5 and 10 % CNC the mass loss presents about the same value as for the blends without CNC. The residual mass at 700 °C is also comparable with the residual mass for simple PVA/S blends.

The differences observed for the behavior of the PVA/S and PVA/S/CNC blends allows the conclusion that both S and CNC increase the thermal stability of PVA and the blends components influence each other during decomposition.

The overall kinetic parameters for the thermal decomposition of the studied samples obtained by the Coats-Redfern method are given in Table 3.

Table 3

Overall kinetic parameters of the PVA/S and PVA/S/CNC blends evaluated by the Coats-Redfern method

Sample	Step I (25-110°C)		Step II (110-250°C)		Step III (250-370°C)		Step IV (370-520°C)	
	Ea kJ/mol	n	Ea kJ/mol	n	Ea kJ/mol	n	Ea kJ/mol	n
PVA	90.3	1.5	132.7	1.7	172.6	2	309.2	2.1
S	89.1	2.1	91.1	1.4	273.6	2	160.2	1.9
50%PVA/50%S	77.9	1.8	107.4	1.7	131.6	1.7	341.1	2
75%PVA/25%S	95.7	1.4	128.2	1.9	151.5	1.6	277.4	1.8
90%PVA/10%S	80.3	1.3	155.8	2.1	164.9	1.8	185.6	1.6
5 % CNC	111.5	1.4	152.0	2	175.3	1.9	305.7	2.3
10% CNC	117.2	1.6	137.1	1.9	179.7	1.9	355.6	2.7
15 % CNC	91.7	1.4	123.1	1.7	133.4	1.4	412.1	1.8
CNC	123.5	1.9	81.7	1.5	-	-	114.2	1.8

For the first decomposition stage of PVA/S films, the reaction order varies between 1.3 and 2.1 and the overall activation energy between 79 kJ/mol and 96 kJ/mol. The values corresponding to both parameters increase with increasing S content in the blends. For the second and third decomposition stages, the activation energy and the reaction order decrease with increasing the S content from 2.1 to 1.4 and 156 kJ/mol-107 kJ/mol in case of stage two and 2-1.6 and 173-132 kJ/mol in stage three, respectively. In the last decomposition stage the activation order is situated in the 2.1-1.6 range and the overall activation energy between 342-187 kJ/mol. In this case, the activation energy for the blends is higher than that for the pure components. This behaviour could be explained by some important changes. The morphology of the blend is highly different in respect with those of the components, so that the water and other low molecular weight compounds are easily eliminated, while at higher temperature a new, more thermally stable structure is formed through interactions between the components whose decomposition occurs through a different mechanism.

For the blends containing CNC, in the case of the first, third and fourth stages the activation energy increases with the increase of the CNC content up to 10 wt% and decrease for the blend with 15 wt% CNC. The activation energy for the second stage decreases for all studied samples from 155 kJ/mol in PVA/S film to 82 kJ/mol in CNC. The incorporation of the rigid CNC moieties in the PVA/S blends probably induces an orientation of the polymeric molecules and favours the formation of H bonds between the polymeric chains.

CONCLUSIONS

Thermogravimetric curves clearly showed the shifting of major degradation decomposition stages to higher temperatures, suggesting the increased thermal stability for all studied blends in comparison to their sole component materials. The higher crystallinity of the cellulose nanocrystal samples compared to the used biopolymers might be the reason explaining the increased thermal stability.

The inclusion of cellulose nanocrystals resulted in an increase of the degradation temperature of nanocomposites, indicating a higher thermal stability of nanocrystals and restriction of the

mobility of polymer chains caused by the homogenous distribution of cellulose nanofibers in the matrix.

The activation energy for the main decomposition stages of the blends containing PVA and S decreases with increasing S content. For the blends containing CNC, the energy corresponding to the third and fourth decomposition stages increases with increasing the CNC content and are higher than those corresponding to the pure components. This may suggest the formation of strong H bonds between CNC and the polymeric matrix.

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