Thermal and Thermo-Oxidative Degradations of Polyvinyl Alcohol with 2,5-Furandicarboxylic Acid Acting as a Crosslinking

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Abstract

The study assesses the thermal and thermo-oxidative for poly(vinyl alcohol) (PVA) with 2,5-furandicarboxylic acid (FDCA) acting as a crosslinking. PVA-crosslinked-FDCA were synthesized via catalyst-free solid-state esterification at 120 °C. PVA and FDCA with different contents of inorganic phase (1, 5, and 10 % (w/w)) were characterized by Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy. The thermal degradation of the obtained products was studied by Thermal Gravimetric Analysis/ Differential Thermal Gravimetric Analysis under air and nitrogen atmosphere. The effect of FDCA content on thermal and thermo-oxidative stability of PVA was discussed. The thermal stability of PVA was significantly improved, particularly at low FDCA concentrations of 1% and 5%. In these cases, the degradation maximums occurred at 361 °C and 375 °C, respectively, compared to 300 °C for unmodified PVA in a nitrogen atmosphere. Moreover, the degradation maximums occurred at 363 °C and 399 °C, respectively, compared to 337°C for unmodified PVA in an air atmosphere. In addition, thermal stability of the films under air is even better than that under nitrogen atmosphere.

Keywords: Polyvinyl alcohol, 2,5-furandicarboxylic acid, crosslinking.

1. Introduction

In recent times there is growing interest in developing materials with biodegradable capacity to achieve a healthy environment in the near future [1]. The utilization of biodegradable products has been one of the promising approaches to tackle the issues of plastic pollution, as well as to facilitate current waste management [2]. Among different kinds of biodegradable polymers, poly(vinyl alcohol) (PVA) has attracted significant attention because of many desirable characteristics (excellent film forming, emulsifying and adhesive properties, resistance to oil and grease, odorless, nontoxic) [3]. PVA can be used in a wide range of applications such as fabric and paper sizing, fiber coatings, adhesives, emulsion polymerization, packaging, and agricultural films [4]. However, further expansion of PVA applications is limited due to the hydrophilic nature of PVA which causes film swelling, poor moisture barrier and mechanical properties [5]. There are many applications for PVA-based water-resistant films (mainly in the packaging field and optoelectronic field) and applications as engineered blood vessels [5, 6].

To overcome the disadvantage of PVA's high level of water absorption, a crosslinker is employed to form linkage between the hydroxyl group of PVA and bio-based substances. PVA's crosslinked structure can be achieved through the formation of covalent bonds between polymer chains. The formation of crosslinks enhances water absorption resistance, separation ability, as well as thermal and mechanical properties.

A potential crosslinker is 2,5-furandicarboxylic acid (FDCA), a good precursor of two carboxylic acid groups attached to a central furan ring. FDCA is a versatile biobased building block synthesized from 5-hydroxymethylfurfural (HMF), a biological precursor that can be synthesized directly from biomass such as sugar, starch, and cellulose [7]. The structural similarity of FDCA to the very common petrochemical monomer terephthalic acid, has made FDCA a popular biobased alternative with comparable properties [8]. Studies suggest that FDCA-derived polyester has barrier properties higher than their terephthalic acid-based counterparts. In addition, as a diacid, FDCA can be employed as a crosslinking agent to enhance the properties of PVA. The presence of furan rings in the PVA structure is expected to have a remarkably positive effect on the thermal and mechanical properties of the product.

Recently, PVA was crosslinked with FDCA by solution casting method to obtain different PVA/FDCA membranes. The optimal crosslinking agent concentration, reaction time, thermal and mechanical properties were examined [9]. However, there are few reports about the effect of cross-linking

agents on the thermal and thermo-oxidative stabilities of PVA. High thermal stability is a crucial characteristic for industrial applications. The presence of oxygen can impact the thermal stability of materials. Therefore, the thermal degradation behavior was investigated using Thermal Gravimetric Analysis/ Differential Thermal Gravimetric Analysis (TGA/DTGA) in both nitrogen and air atmospheres.

In this study, the objective was the investigation of the thermo-oxidative destruction of PVA-crosslinked-FDCA by simultaneous TGA/DTGA analysis. And the formation of ester crosslinks between PVA and FDCA was analyzed using Attenuated Total Reflection-Fourier transform infrared spectroscopy (ATR-FTIR).

2. Experiment

2.1. Materials

PVA (CAS: 9002-89-5) (degree of polymerization, 1750 ± 50; degree of hydrolysis, 99%) was purchased from Shanghai Zhanyun Chemical Co., Ltd (China). The hydrolysis degree of PVA was obtained from ^{1}H NMR. FDCA (CAS: 3238-49-2) was provided by Sigma-Aldrich (USA). DMSO (CAS: 67-68-5) was procured from Merck (Germany). Other chemical products were also purchased from Sigma-Aldrich (USA).

2.2. Methods

As seen in Fig. 1, The crosslinking PVA was achieved using FDCA as a crosslinker through solution casting method. Solutions of PVA (5%, w/w) were prepared by dissolving PVA by magnetic stirring in dimethylsulfoxide (DMSO) at 50 °C for 6 h. FDCA/DMSO solutions were added and continued to be stirred for 2 h at room temperature. Different acid concentrations (0, 1, 5, and 10% (w/w)) concerning PVA were used. To avoid the formation of PVA lumps, the solutions were mechanically stirred for 30 min at room temperature. The solutions were cast in a petri dish and dried in a heating oven at 50 °C for 72 h. The completely dried FDCA/PVA films were crosslinked by heating at 120 °C in an oven for 2 h to obtain the PVA-crosslinked-FDCA films.

These films were then stored in a desiccator at ambient temperature to avoid moisture uptake. Before sample characterization, all samples were equilibrated at 25 °C and 50% relative humidity (RH) before the measurements.

2.3. Characterization of Films

FTIR: Infrared spectra of samples were recorded on a Nicolet iS50 FTIR (Thermo Fisher Scientific) spectrometer in Attenuated Total Reflection mode. The specimens were measured directly with a scan range from 400 cm^{-1} to 4000 cm^{-1}.

TGA and DTGA: The experiments were performed using a NETZSCH STA 449F5 analyzer with a heating rate of 10 °C/min under nitrogen and air atmospheres and a temperature scan of 25 - 600 °C.
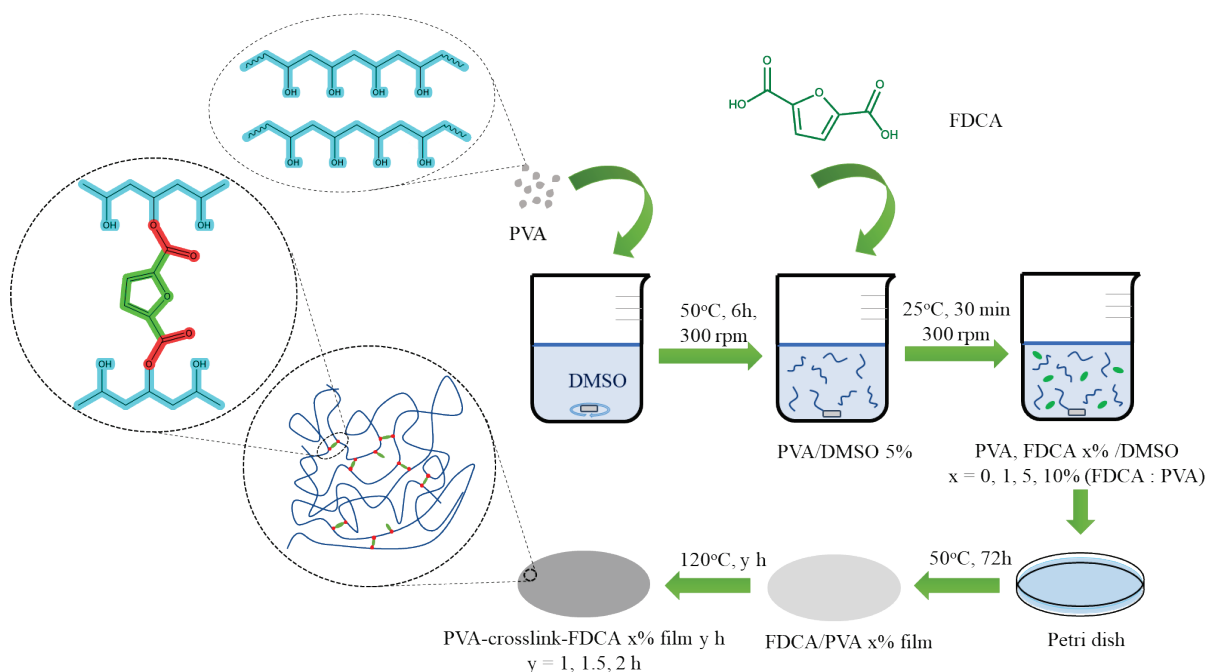

Fig. 1. Schematic overview of PVA-crosslinked-FDCA preparation

3. Result and Discussion

3.1. Confirmation of the Structure of the PVA-Crosslinked-FDCA Films

The FTIR spectra of PVA and PVA-crosslink-FDCA 5% are shown in Fig. 2. Characteristic signals obtained from IR data of pure PVA and PVA-crosslinked-FDCA 5% films are shown in Table 1.
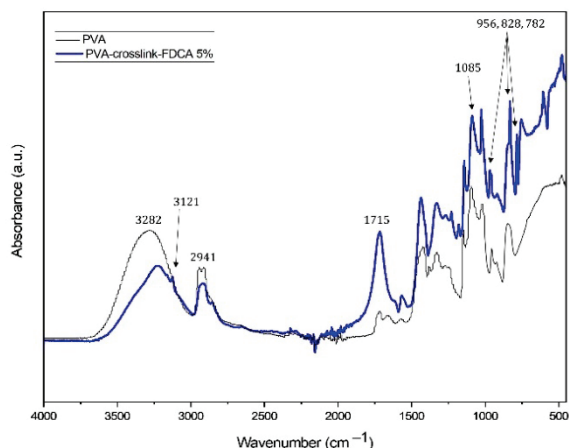

Fig. 2. ATR-FTIR spectra of PVA and PVA-crosslinked-FDCA 5%

From the FTIR spectra of PVA, the absorption band from 3200 to 3500 cm^{-1} was attributed to the stretching vibration of hydroxyl -OH groups. This indicates the presence of hydrogen bonding between the -OH groups within the PVA chains. The stretching vibration of C_{sp3}-H bonds, including -CH and -CH$_2$ stretching of PVA, was detected at 2941 cm^{-1}. A peak at 1085 cm^{-1} was the C-O stretching vibration, while an absorption signal at 1715 cm^{-1} was attributed to carbonyl C=O stretching vibration. The slight absorption of C=O corresponded to residual acetate groups, which remained after the incomplete hydrolysis of poly(vinyl acetate)

The spectra of PVA-crosslinked-FDCA 5% samples exhibited similar signals to those of PVA. However, there was a decrease in the intensity of the O-H signal, suggesting a reduction in the interaction of hydrogen bonds among -OH groups. In addition, the intensity of the characteristic signal of C=O groups at 1715 cm^{-1} increased in comparison to the corresponding signal of PVA. Thus, the changes in intensities and positions of the absorption signals of

the O-H and C=O groups in the FTIR spectra confirmed the formation of ester crosslinks between the hydroxyl groups of PVA and carboxyl groups of FDCA. The IR spectra also showed the presence of furan rings in the modified polymer, as evidenced by signals such as the vibration of C_{furan}-H at approximately 3121 cm^{-1} and bending motions of furan at 956, 828, and 782 cm^{-1}.

The FTIR spectra of PVA-crosslinked-FDCA samples exhibited noticeable variations at different concentrations of FDCA (Fig. 3). The spectrum for the 1% FDCA sample was identical to that for PVA. Meanwhile, the spectrum of the 10% FDCA sample showed a broad absorption band between 2400 and 3600 cm^{-1}. This absorption band was attributed to the absorption of carboxyl groups in the carboxylic acid dimers, which could be explained by the low solubility of FDCA in PVA. At high concentrations, FDCA could aggregate to form its phase and not participate in the crosslinking reaction [10]. The presence of FCDA aggregates resulted in the appearance of a broad absorption band between 2400 and 3600 cm^{-1}.
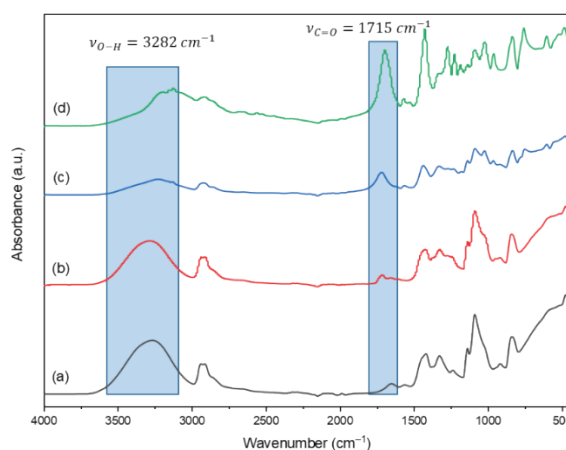

Fig. 3. ATR-FTIR spectra of (a) PVA and the prepared films, (b) PVA-crosslinked-FDCA 1%, (c) 5%, and (d) 10%

The ratios between the carbonyl band at 1715 cm^{-1} and the hydroxyl band at 3282 cm^{-1} increased with increasing concentrations of FDCA in the crosslinked PVA samples. In the PVA sample, the ratio was 0.208. However, the ratios for the PVA-crosslinked-FDCA 1%, PVA-crosslinked-FDCA 5%,

Table 1. Characteristic signals obtained from IR data of pure PVA and PVA-crosslinked-FDCA 5% films.

Bond	PVA	PVA-crosslinked-FDCA
O-H	3282 cm^{-1}	3226 cm^{-1}
C-H furan	-	3121 cm^{-1}
C_{sp3}-H	2941 cm^{-1}	2941 cm^{-1}
C=O	1715 cm^{-1}	1715 cm^{-1}
C-O	1085 cm^{-1}	1085 cm^{-1}
Bending motions of furan	-	956, 828, 782 cm^{-1}

and PVA-crosslinked-FDCA 10% samples were 0.241, 1.168, and 3.466, respectively. These results provide further evidence of the formation of crosslinking ester bonds between the hydroxyl group of PVA and the carboxyl group of FDCA, as the number of -OH groups decreased and the number of C=O ester groups increased with higher FDCA concentrations.

3.2. Thermal Properties

As we know, the processing of polymers was usually conducted in the air atmosphere. The information about the thermal stability of the PVA polymer and the effect of FDCA on its stability was obtained from TGA measurements in inert and air atmospheres. Thermal decomposition in an inert atmosphere of neat PVA and FDCA/PVA with different FDCA content are presented in Fig. 4 and 5. The main thermogravimetric characteristics obtained from the analysis of the TGA and DTGA curves are presented in Table 2. The degradation of PVA is reported to be a three-stage degradation mechanism in nitrogen [11]. An early weight loss process in the temperature range of 30 - 160 °C with a weight loss of 7.3% is attributed to the evaporation of bound and non-bound water molecules in PVA. The second stage with weight loss of 72.5% is dominated by chain-scission reactions, side reactions and cyclization reactions [11]. The third decomposition step was observed with a maximum of 420 °C with weight loss of 10.9% and was associated with chain scissions of polyenes and intramolecular cyclization [11].
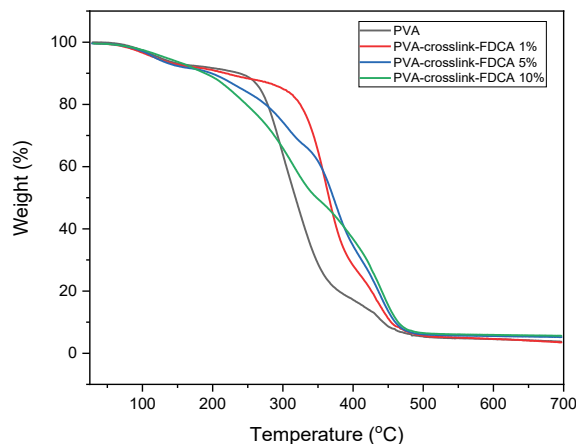

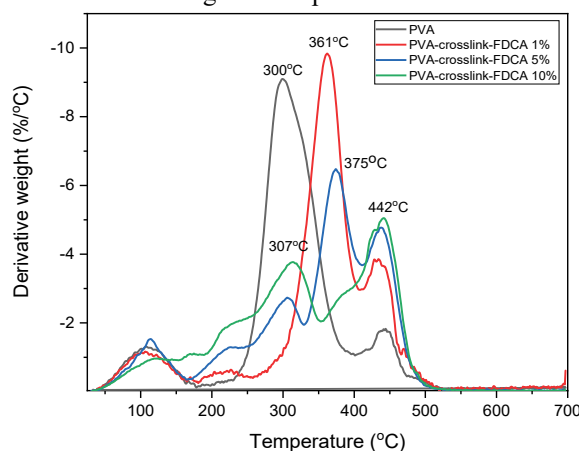Fig. 4. TGA curves of PVA and PVA-crosslinked-FDCA under nitrogen atmosphere

Fig. 5. DTGA curves of PVA and PVA-crosslinked-FDCA under nitrogen atmosphere

Table 2. TGA data of PVA and PVA-crosslinked-FDCA samples

Sample	Decomposition step	Temperature range (°C)		Maximum temperature (T_{max}) (°C)		Weight loss (%)	
		N₂	Air	N₂	Air	N₂	Air
PVA	1st	30-160	30-160	107	100	7.3	9.3
	2nd	240-400	260-400	300	337	72.5	52.5
	3rd	400-470	400-480	442	442	10.9	19.4
	4th	-	480-570	-	496	-	9.8
PVA-crosslink-FDCA 1%	1st	30-160	30-170	106	125	7.3	6.2
	2nd	300-410	260-400	361	363	60.6	52.3
	3rd	410-470	400-480	434	427	17.4	24.0
	4th	-	480-600	-	500	-	11.8
PVA-crosslink-FDCA 5%	1st	30-160	30-160	120	96	8.2	6.9
	2nd	220-330	250-340	307	312	21.1	21.6
	3rd	330-410	340-380	375	375	35.1	10.9
	4th	410-500	380-470	439	399	25.2	36.6
	5th	-	470-550	-	505	-	13.4
PVA-crosslink-FDCA 10%	1st	30-170	30-170	122	124	8.5	6.4
	2nd	210-350	250-350	312	312	37.3	29.7
	3rd	350-500	390-480	442	421	43.8	31.5
	4th	-	480-540	-	516	-	13.0

The presence of 1% FDCA in films does not affect the degradation mechanism itself but influences on overall thermal stability of the PVA matrix. In the first stage up to 160 °C, there are attributed to loss of bonded/or physically absorbed water. The significant weight loss is the second step observed in the 300 - 410 °C range, which may be responsible for the structural decomposition of the PVA. Maximum decomposition for this stage was observed at higher temperatures (T_{max} = 361 °C) compared to PVA (T_{max} = 300 °C). The third occurs at temperature range of 410 - 470 °C that represents the completion of the decomposition of the remaining polymer residues along with the carbonization.

When 5% FDCA concentrations were incorporated, the film exhibited three weight-loss stages similar to pure PVA. Furthermore, an additional decomposition peak emerged between the previously mentioned second and third stages. Consistent with the degradation pattern of PVA, an initial minor weight loss occurred between 30 °C and 160 °C, attributed to the evaporation of water molecules. The second stage in the 200 - 300 °C range corresponded to dehydration, deacetylation, and chain scissions, converting these free polymer chains to low-molecular-weight polyenes was observed to a lesser extent. Therefore, the weight loss during this period was slight with weight loss of 21.1% rather than 72.5% in case of PVA, and the decomposition maximum also increased slightly compared to PVA (307 °C). The main degradation maxima of PVA-crosslinked-FDCA 5% occurred at 375 °C. The decomposition associated with this stage was due to the cleavage of FDCA crosslinks and C-C bonds of main chains to convert most of the crosslinked polymer to gaseous products [12]. The final stage between 400 - 500 °C was also the complete decomposition of remaining polymer residues and the carbonization.

The decomposition pattern of PVA-crosslinked-FDCA 10% differed from the other two concentrations. Almost no additional degradation stage was observed when compared to PVA, and more weight was lost in the 210 - 350 °C region with weight loss of 37.3% compared to 5% FDCA sample with weight loss of 21.1%. A high density of crosslinks was formed, especially with highly rigid FDCA molecules, some PVA chains were kept at unstable conformations after crosslinking. These chains were susceptible to chain scission in the early stage of the degradation, which generated free radicals and initiated further propagating chain cleavage.

Fig. 6 and 7 shows the TGA and DTGA for PVA and PVA-crosslinked-FDCA samples performed in air. The main thermogravimetric characteristics obtained from the analysis of the TGA and DTGA curves are presented in Table 2.
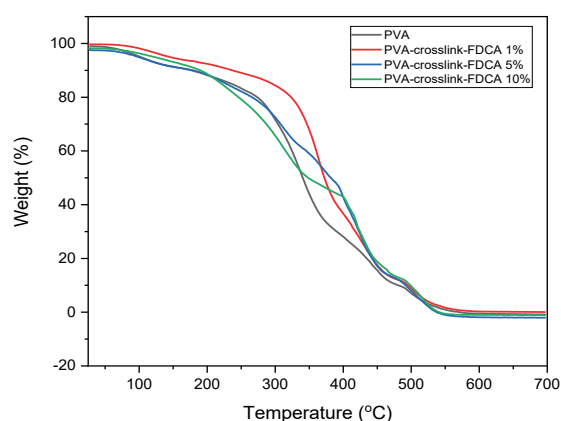

Fig. 6. TGA curves of PVA and PVA-crosslinked-FDCA under air atmosphere
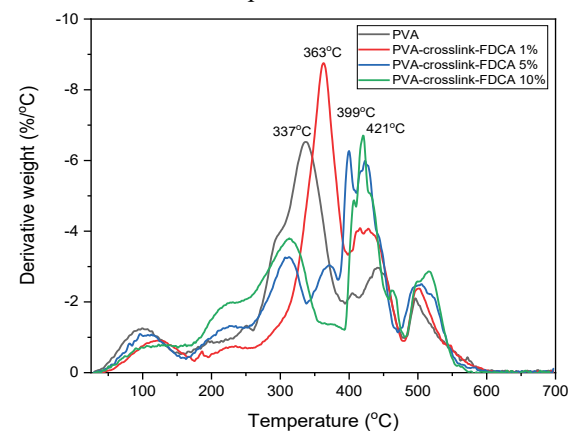

Fig. 7. DTGA curves of PVA and PVA-crosslinked-FDCA under air atmosphere

The thermo-oxidation of PVA occurs through four successive processes with the formation of volatile compounds. In the first process, around 100 °C loss of bonded/or physically absorbed water can be observed. This process is followed by three complex processes. First, there is partial dehydration of PVA accompanied by the formation of polyenes in the temperature range of 300 - 350 °C. In the next stage, these polyenes undergo decomposition, primarily at the α position of the tertiary carbon atom, resulting in the formation of macroradicals. The degradation of these macroradicals yields low-molecular-weight oxygen-containing products, such as acetaldehyde, benzaldehyde, acrolein, and others. Additionally, during this stage, polyene macroradicals decompose into cis-trans derivatives, whose latter results in the formation of polyconjugate aromatic structures through intramolecular cyclization and condensation, according to the Diels-Alder mechanism (~450 °C). Finally, the process of thermo-oxidation of the carbonized residue occurs in the temperature range of 480 - 550 °C [3].

The TGA curves of FDCA/PVA samples are also characterized by four weight loss stages as pure PVA. However, the maximum mass loss rates of the FDCA/PVA composites shifted to a higher

temperature. The PVA-crosslinked-FDCA 1% film exhibits enhanced thermo-oxidative stability above 363 °C compared to pure PVA (337 °C). Similarly, to the degradation pattern of PVA in an inert atmosphere, in the case of 5% FDCA concentration, there was an additional decomposition peak with weight loss of 10.9% appeared between the respective second and third stages of PVA. The pyrolysis of ester bonds takes place in the PVA-crosslinked-FDCA film, generating active free radicals that promote thermo-oxidative decomposition within the main molecular chain[13]. However, the majority of weight loss for the samples occurs between the temperature range of 380 °C and 470 °C, reaching a maximum temperature (T_{max}) of 399 °C, and resulting in an approximate weight loss of 36.6%. Similarly, for the PVA-crosslinked-FDCA 10% sample, most of the mass is lost within the same temperature range, with a T_{max} of 421 °C and an approximate weight loss of 31.5%. This results from the thermo-oxidative degradation of the furan ring in the main molecular chain[13]. Noticeably, as the FDCA concentration increases, the composites leave behind a greater amount of residual char, resulting in a 4, 9, and 20 °C increase in thermo-oxidative stability for PVA films with 1, 5, and 10% (w/w) FDCA, respectively (Table 2).

A comparison between the two atmospheres revealed that the thermal stability of the films was superior under air compared to the nitrogen atmosphere. Specifically, the maximum thermal stability temperatures with the loss of most of the products' weights in the air for PVA, PVA-crosslinked-FDCA 1%, PVA-crosslinked-FDCA 5% were 337, 363 and 399 °C, respectively. However, in the nitrogen atmosphere, these values reduced to only 300, 361 and 375 °C, respectively. This difference in thermal stability can be attributed to the presence of an electron donor (C=O) that captures oxygen and active free radicals generated during the initial stage of thermal oxygen degradation, leading to molecular rearrangement and the formation of a more stable structure[14]. Additionally, non-combustible volatiles (such as CO_2 and H_2O) are produced and released, that can absorb heat and isolate intermediate products, thereby delaying further degradation [14]. However, PVA-crosslinked-FDCA perform excellent thermal stability, whether under nitrogen or air atmospheres.

4. Conclusion

The influence of crosslinking agents on the structure and thermal properties of PVA was investigated. The thermal analysis of PVA and PVA-crosslinked-FDCA through comparison with the thermal behavior of its components. The incorporation of FDCA into the PVA matrix increased thermal degradation and thermo-oxidative stability to some extent due to the formation of covalent bonds, but the improvements depend on FDCA concentration. The decomposition environment (air or nitrogen) does not significantly influence thermal degradation pattern for PVA and PVA-crosslinked-FDCA samples.

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