THERMAL PROPERTIES OF POLY(2-ISOPROPENYL-2-OXAZOLINE) CROSSLINKED NETWORKS

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Poly(2-isopropenyl-2-oxazoline) (PiPOx) networks crosslinked with amino and hydroxy dicarboxylic acids were synthesized and their thermal properties, and thermal decomposition mechanisms were analyzed using TGA-DSC-MS technique. Crosslinking improved the thermal stability of PiPOx networks, with stability being influenced by the chemical structure of the crosslinker. DSC analysis showed that PiPOx xerogels did not exhibit a T_g but displayed broad exothermic transitions above 220 °C due to structural rearrangements or chemical reactions. The mass spectrometry indicated distinct degradation pathways dependent on the functional groups present in the crosslinker. The PiPOx xerogels showed excellent thermal stability being suitable for high-temperature sterilization in medical applications.

Keywords: xerogels, poly(2-isopropenyl-2-oxazoline), hydrogels, thermal characterization

1. Introduction

Hydrogels are three-dimensional hydrophilic polymeric networks that exhibit a remarkable capacity to absorb substantial quantities of water or other physiological fluids owing to their inherent hydrophilic properties. [1]. Due to

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their high water uptake and soft texture, hydrogels exhibit a strong similarity to the living tissue being extensively investigated and used in the biomedical field.[2] Moreover, hydrogels have very good permeability for oxygen, nutrients, and other water soluble metabolites, making them ideal carriers for therapeutic agents including small drugs, proteins and even cells. [3] Common synthetic monomers and polymers used for the synthesis of hydrogels include but are not limited to acrylamide [4], acrylic acid, vinylpyrrolidone [5], 2-hydroxyethyl methacrylate [6], poly(ethylene glycol) [7], poly(vinyl alcohol) [8] and poly(2-oxazoline)s [9].

Recently, poly(2-isopropenyl-2-oxazoline) (PiPOx) has emerged as a versatile polymer platform for creating various hydrogel materials. [10] The versatility of PiPOx stems from its reactive 2-oxazoline side chain groups that allow for straightforward modification reactions with carboxylic acids, offering a robust chemistry to customize a wide range of physicochemical properties for specific applications. [11] PiPOx was successfully used for the synthesis of a wide variety of materials, including smart polymers [12-14], responsive hydrogels [15, 16], nanofibers [17], and microparticles [18]. In our previous work we reported the synthesis of poly(2-isopropenyl-2-oxazoline) (PiPOx) degradable hydrogels crosslinked with various hydroxy/amino dicarboxylic acids. [15] The hydrogels showed susceptibility to hydrolytic degradation and their potential for drug delivery applications was demonstrated using propranolol hydrochloride as a model drug. Moreover, the hydrogels and their degradation products were noncytotoxic and did not promote inflammatory responses or thrombosis. In addition to assessing swelling behavior and mechanical properties, it is important to investigate the thermal stability of these hydrogels. The thermal characterization can provide important insights regarding long term storage in the dry state (xerogels), sterilization procedures to be used, identifying any potentially toxic degradation products and on the physical state of the polymer network (i.e., rubbery, glassy, or semicrystalline) which strongly influences the drug release behavior.

Thus, the present work aims to investigate the thermal properties of PiPOx crosslinked networks. Simultaneous thermogravimetric analysis coupled to mass spectrometry (TGA-DSC-MS) was used to investigate the thermal stability, phase transitions and thermal decomposition process of the dry hydrogels (xerogels).

2. Experimental

2.1. Materials

The succinic acid (99+%, Suc), and *DL*-cysteine hydrochloride (98+%, Cys) from Alfa Aesar, and *DL*-malic acid (99%, Mal), *DL*-tartaric acid (99%, Tar), aspartic-*DL*-acid (99%, Asp), glutamic-*L*-acid (99+%, Glu), and Sigmacote

all from Sigma-Aldrich were used as such. PiPOx (DP = 250) was prepared via living anionic polymerization using the optimized protocols reported in our previous work. [19] The amino acid hydrochlorides were synthesized by adapting the protocol of van Enckevort [26] as reported in our previous work. [15]

2.2. Characterization

The thermal degradation and glass transition temperatures (T_g) of the xerogels (simultaneous TGA-DSC, MS hyphenated) were measured on a NETZSCH STA 449C Jupiter system, coupled to an Aeolos II MS detector. Degradations were performed in the scanning mode for all samples, from ambient temperature up to 750 °C, at a heating rate of 10 °C/min under helium flow (25 ml/min). The background at a temperature below the onset of degradation was subtracted from each MS spectrum to account for signals present due to impurities found in the carrier gas. Prior to the thermogravimetric analysis, the xerogels were dried under vacuum in a drying oven at 60 °C for 24 hours.

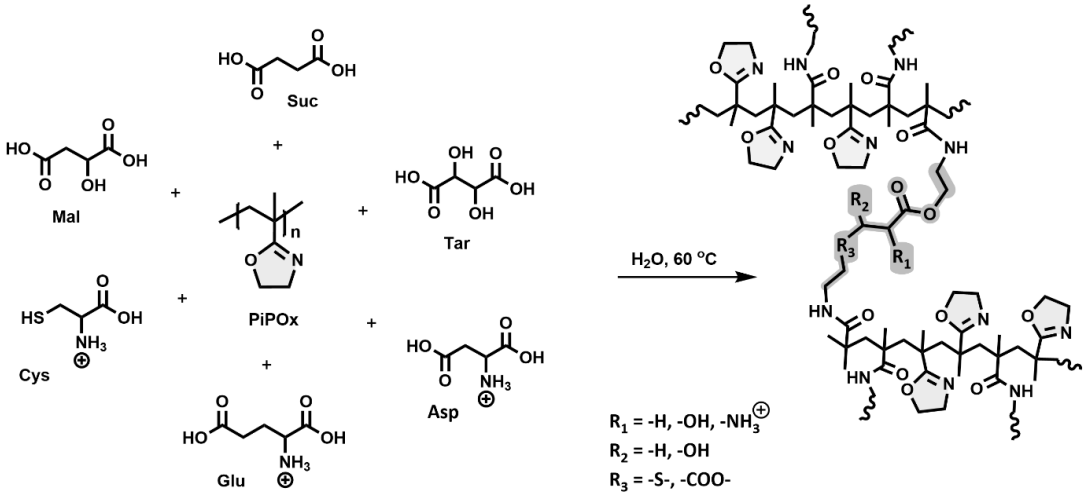
2.3. Synthesis of PiPOx-based hydrogels

The PiPOx-based hydrogels were synthesized according to our previously reported method. [15] The hydrogels disks were dried at room temperature until a constant mass was reached to obtain xerogels.

3. Results and discussion

PiPOx xerogels were synthesized by crosslinking the side-chain 2-oxazoline groups of PiPOx with succinic acid (Suc), malic acid (Mal), tartaric acid (Tar), cysteine hydrochloride (Cys), aspartic hydrochloride acid (Asp), and glutamic hydrochloride acid (Glu) (see Scheme 1). The crosslinking reactions were performed in distilled water at 60 °C under catalyst-free conditions using a previous reported protocol developed by our group. [15] In all experiments a molar ratio of iPOx:COOH of 1:0.1 and a 20 wt %/ polymer concentration were used.

The thermal properties of the synthesized xerogels were analyzed using differential scanning calorimetry (DSC) and thermogravimetric analysis coupled with mass spectrometry (TGA-MS). DSC was employed to examine the thermal transitions, such as melting and/or glass transitions, while TGA was used to assess the thermal stability and decomposition profiles of the xerogels. The thermograms showing the degradation behavior are presented in Fig. 1 and the main thermogravimetric characteristics such as T_{d10} - the temperature at which the weight loss is 10%, T_{max} - the temperature at which the thermal degradation is the highest, and residual mass are given in Table 1.



Scheme 1. Reaction route for the synthesis of PiPOx hydrogels crosslinked with functional dicarboxylic acids.

The thermal stability of the xerogels increased by almost 50 °C compared to the uncrosslinked PiPOx polymer. This improvement in thermal stability can be attributed to the crosslinking process, which limits the mobility of polymer chains, thereby increasing the activation energy of the onset of thermal degradation.

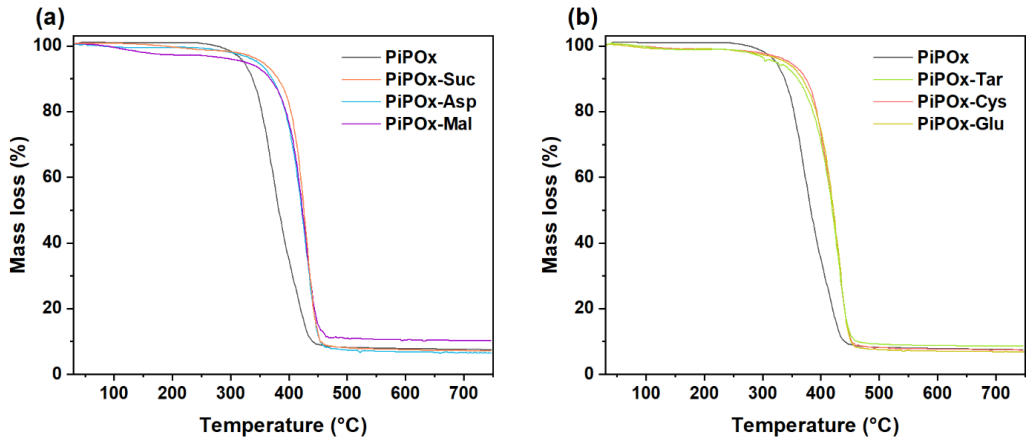


Fig. 1. TGA profiles for PiPOx and PiPOx-based xerogels.

The crosslinker's chemical structure did not substantially influence the thermal degradation temperature (T_d) of the xerogels. However, when comparing PiPOx-Suc with other xerogels, one can observe that the presence of functional groups within the crosslinker slightly reduces thermal stability (see Table 1). Specifically, PiPOx hydrogels crosslinked with amino acids exhibited lower thermal stability than PiPOx-Suc, with a decrease of approximately 10 °C in T_d. This reduction in stability can be attributed to the lower thermal stability of the

ester bond at the α-carbon of the amino acid, due to the presence of charged amino groups. The length of the crosslinker had a minimal impact on the thermal stability, as the T_d of PiPOx-Asp was only 3 °C higher than that of PiPOx-Glu. However, a more pronounced decrease in thermal stability was observed in the case of xerogels crosslinked with malic or tartaric acid. This behavior is due to the inherent thermal instability of tartrate and malate esters, which are more susceptible to degradation by heat.

Table 1

Thermogravimetric parameters and thermal transitions of PiPOx xerogels

Sample	T_{d10} (%)[a]	T_{max} (°C)[b]	Residue at 700 °C (%)
PiPOx	337.7	370.4	7.6
PiPOx-Suc	381.5	431.1	7.2
PiPOx-Asp	371.5	430.2	6.7
PiPOx-Glu	368	430.6	6.9
PiPOx-Cys	374.1	431.2	7.5
PiPOx-Mal	367.7	429.6	10.3
PiPOx-Tar	360.1	428.8	8.6

[a]Temperature represents 10% weight loss in TGA measurements at heating rate of 10 °C/min.
[b]Temperature corresponding to the maximal degradation rate.

The char residues measured for PiPOx-Mal and PiPOx-Tar are higher than in the other xerogels (Table 1), indicating that the presence of hydroxyl groups within the crosslinker structure enhances secondary reactions. These reactions favor the formation of carbonaceous residues rather than leading to breakdown into volatile components.

The PiPOx polymer showed the characteristic glass transition temperature (T_g) at 178 °C [20, 21] (Fig. 2a). In contrast, the xerogels displayed no significant T_g during DSC analysis up to the onset of thermal degradation. The absence of a T_g can be attributed to the presence of crosslinking points, which severely restricts the mobility of the polymer chains. However, all xerogels except PiPOx-Cys exhibited a broad exothermic transition beginning above 220 °C, which occurred well below the onset of thermal degradation (Fig. 2a). The absence of a corresponding weight loss in the TGA analysis of this exotherm in the DSC data suggests that the observed thermal event is not associated with mass loss but rather with structural or chemical rearrangements within the xerogel network that can be attributed to either polymer chain reorganization or crosslinking reactions. The polymer chain reorganization could result from the rearrangement of physical interactions such as hydrogen bonding or ionic interactions within the xerogel structure at high temperatures considering the ester-amide structure formed after the crosslinking reaction (see Scheme 1).

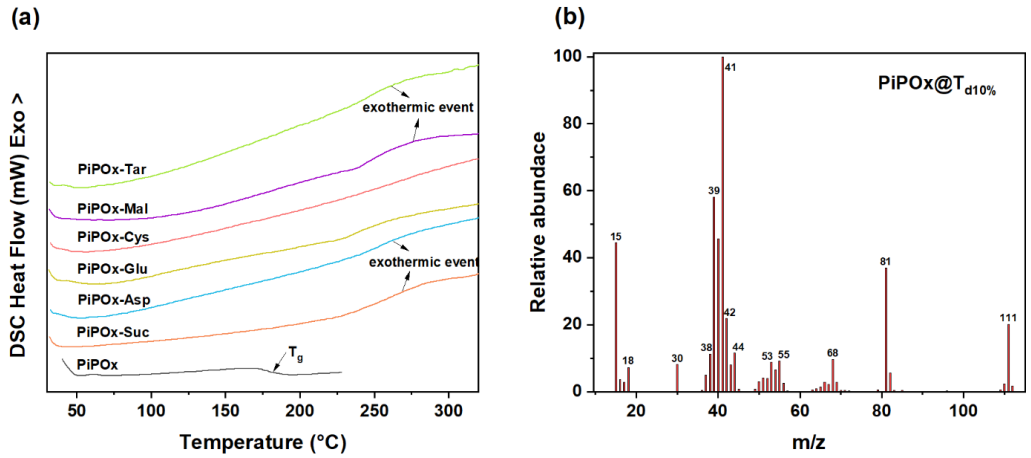


Fig. 2. (a) DSC curves for PiPOx based xerogels and (b) Mass spectrum (MS) of the degradation products of PiPOx at 338 °C.

Alternatively, the exothermic peak may be linked to a cold crystallization process. However, since neither T_g nor a melting temperature was detected below and above this thermal event, respectively, this hypothesis remains uncertain. Another possibility is that the transition originates from additional crosslinking reactions involving unreacted carboxyl groups present at the ends of dangling polymer chains. These free carboxyl groups could potentially participate in further ring opening addition reactions with the unreacted iPOx units at elevated temperatures, leading to an exothermic event. However, this explanation is not supported by the absence of exothermic transition in PiPOx-Cys xerogels. Given the complexity of this thermal behavior, further investigations are necessary to understand its origins fully. Future studies will focus on evaluating the effect of varying heating rates, as well as examining hydrogels crosslinked with different amounts of crosslinker, to provide deeper insights into these thermal transitions.

Further on, insights into the thermal decomposition process of the xerogels were obtained by complementing TGA with mass spectrometry. The mass spectrum of the volatiles that are released at $T_{d10\%}$ upon heating PiPOx reveals the presence of the molecular ion (m/z = 111) suggesting degradation through depolymerization (Fig. 2b). The most significant fragment ions in the spectrum of PiPOx are found at m/z = 15, 39, 40, 41 and 81 corresponding to methyl cations, propene like fragments and 2-oxazoline ring decomposition products, respectively. The PiPOx-Suc xerogel thermal decomposition exhibited different features as compared to PiPOx. The mass spectrum of the volatiles that are released at $T_{d10\%}$, that is 382 °C, is shown in Fig. 3a. The main m/z peaks are: 16, 17, 18, 30, 41 and 44 indicating that the thermal decomposition takes place by the cleavage of the ester bond followed by decarboxylation with elimination of CO_2 (m/z = 44).

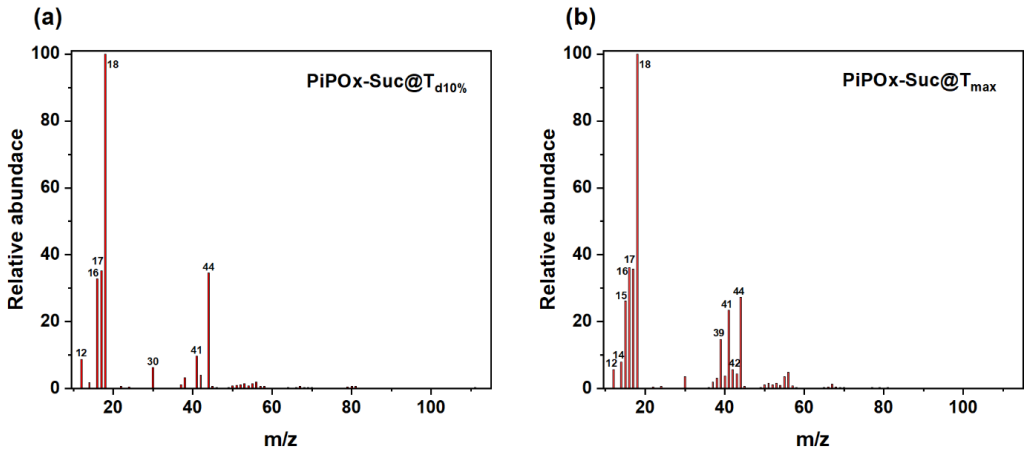


Fig. 3. Mass spectrum (MS) of the degradation products of PiPOx-Suc at (a) 383 °C and at (b) 434°C, respectively.

The signal at m/z = 18 corresponds to the release of water, which can arise from multiple sources such as evaporation of residual or adsorbed moisture, hydrolysis of ester bonds, or dehydration of hydroxyl species. These hydroxyl species may be generated either through the hydrolysis of 2-oxazoline units to form 2-hydroxyethyl methacrylamide units or as a result of ester bond cleavage. The thermal degradation of 2-oxazoline rings leads to the release of ammonia (m/z = 17) as a byproduct. However, this release is observed to occur in significantly higher amounts compared to the uncrosslinked PiPOx polymer (Fig. 2b). Two potential mechanisms can explain this significant increase in ammonia release. First, it may result from the breakdown of amide bonds that are formed during the crosslinking process (Scheme 1). Second, the increase could also be due to the hydrolysis of 2-oxazoline units generated by the residual water at high temperatures. The water present in the sample accelerates the hydrolysis of the 2-oxazoline units, leading to the formation of 2-hydroxyethyl methacrylamide units and/or 2-aminoethyl methacrylate units [22] which subsequently release ammonia. The mass spectrum of the volatiles that are released at T_{max}, that is 434 °C, reveals similar fragments as those observed at $T_{d10\%}$. Notably, one can observe an increase of the signals corresponding to m/z = 15, 39, 41 and 42 suggesting that the degradation of 2-oxazoline units becomes predominant at elevated temperatures while following the same mechanism as observed for the pristine PiPOx polymer. However, no signal at m/z = 111 could be detected indicating that degradation is not occurring through depolymerization in the crosslinked PiPOx networks unlike what is observed in the uncrosslinked ones. The crosslinking process increases the thermal stability of PiPOx polymer by hampering the cleavage of polymer chains into smaller fragments while introducing new degradation pathways that alter the overall fragmentation mechanism.

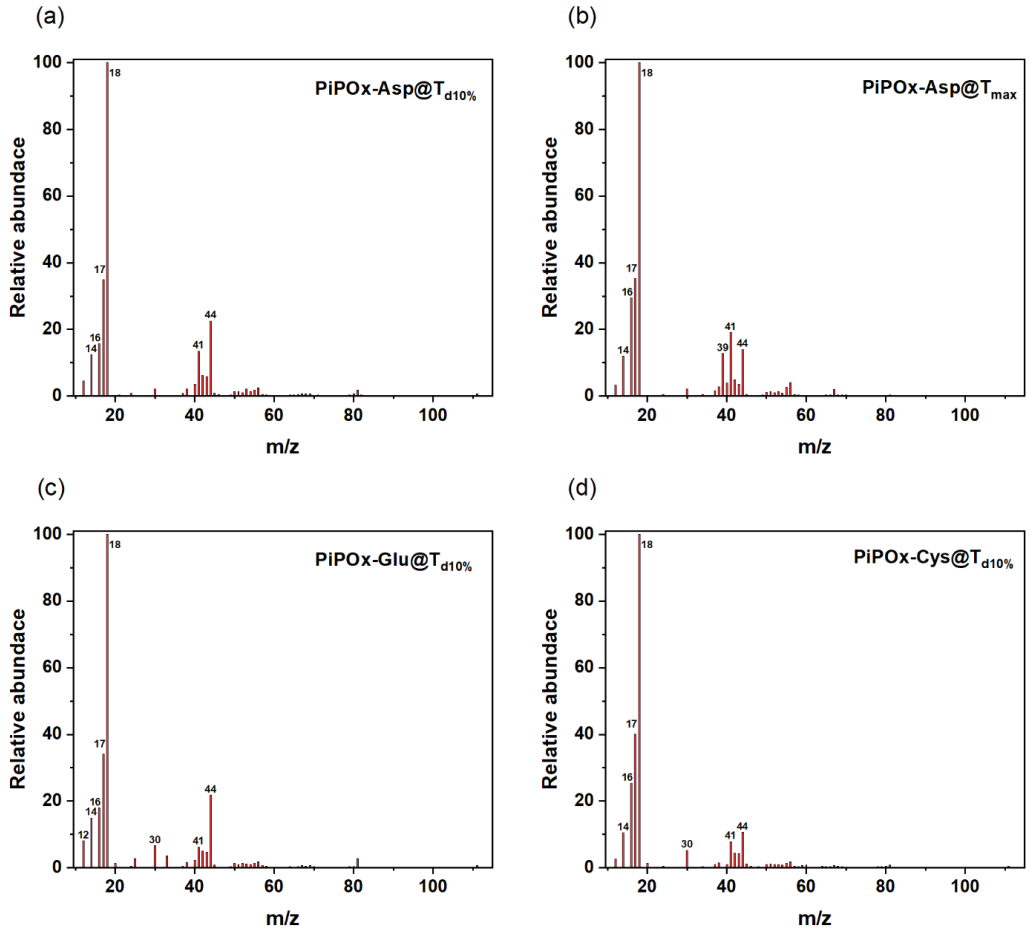


Fig. 4. Mass spectrum (MS) of the degradation products of (a) PiPOx-Asp at 373 °C, (b) PiPOx-Asp at 428 °C (c) PiPOx-Glu at 367 °C and (d) PiPOx-Cys at 378 °C, respectively.

For PiPOx-Asp and PiPOx-Glu the amount of CO_2 released during thermal degradation is notably lower compared to PiPOx-Suc suggesting that in PiPOx networks crosslinked with amino acids, additional reactions beyond simple decarboxylation are occurring (Fig. 4a and 4c). Specifically, dehydration and/or condensation reactions are likely leading to the formation of low organic ester and/or oligoester structures. [23, 24] For PiPOx-Asp a further increase in the temperature, results in an increase of the relative amount of water, while the CO_2 output decreases (Fig. 4b), indicating further degradation of (poly)ester like structures by dehydration into imide structures, a well-known thermal conversion pathway of polyaspartic acid [23, 24], whereas no change in the water to CO_2 ratio with increasing temperature was found in the case of PiPOx-Glu networks (data not shown). Additionally, the presence of the signal m/z = 14 corresponding to either atomic or double ionized nitrogen in the mass spectrum of volatiles from

PiPOx-Asp and PiPOx-Glu (Fig. 4a and 4c), absent in the spectra for PiPOx-Suc (Fig. 3a) or pristine PiPOx (Fig. 2b), provides strong evidence for the incorporation of amino acid-based crosslinkers into the polymer network. Furthermore, the presence of molecular ion fragments of PiPOx (m/z = 111) at $T_{d10\%}$, albeit in very small amounts, suggests that the PiPOx-Asp and PiPOx-Glu networks can undergo some thermal degradation through depolymerization. This depolymerization behavior implies that the crosslinks containing amino groups degrade more rapidly than succinate crosslinks. The faster degradation of the amino containing crosslinks may increase chain mobility and flexibility, destabilizing the network and facilitating depolymerization at elevated temperatures.

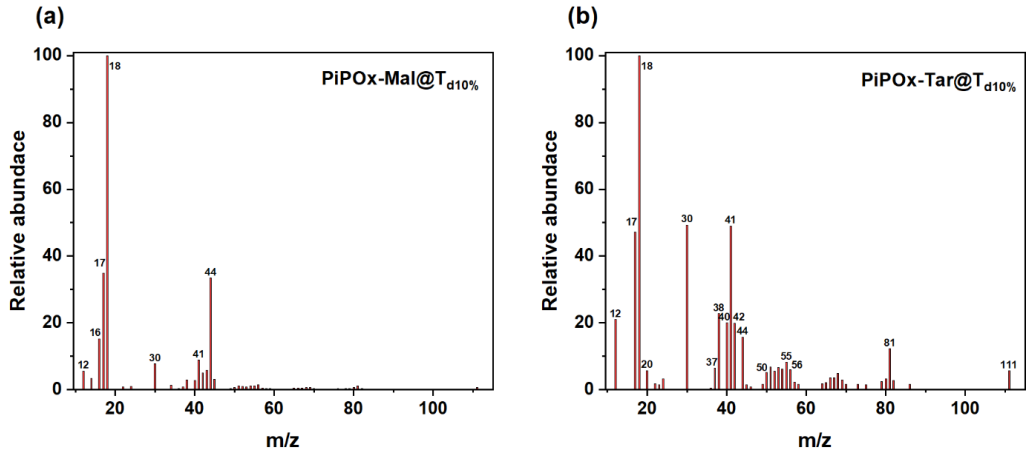


Fig. 5. Mass spectrum (MS) of the degradation products of (a) PiPOx-Mal at 367 °C, and (b) PiPOx-Tar at 361 °C, respectively.

For PiPOx-Mal networks, one can observe the presence of m/z = 111 ion in small amounts (Fig. 5a). The hydroxyl group can enhance thermal decomposition by destabilizing the ester bond, this being supported by the lower $T_{d10\%}$ that is 367.7 °C as compared to the $T_{d10\%}$ of PiPOx-Suc that is 381.5 °C and facilitating the depolymerization process.

Interestingly, even at T_{max}, no signal corresponding to m/z = 28, which would indicate the presence of a CO fragment, was detected (data not shown). Consequently, the degradation pathway does not lead to the direct formation of malic acid, which is typically known to undergo conversion to maleic acid, followed by dehydration to maleic anhydride. [25, 26] Moreover, no molecular peaks corresponding to either maleic acid or maleic anhydride were detected in the mass spectrum of the volatile degradation products. Thus, either no malic acid is generated during thermal degradation or the malic acid along with its degradation products participate in further chemical reactions with the polymer matrix. Most likely, malic acid or its derivatives could react with other functional

groups within the polymer network, primarily with the free iPOx units or via esterification with the 2-hydroxyethyl methacrylamide units resulted from the hydrolysis of iPOx units during degradation. Increasing the number of hydroxyl groups in the crosslinker leads to a dramatic change in the degradation mechanism. The PiPOx-Tar shows clearly the same degradation behavior by depolymerization observed for pristine PiPOx, whereas the CO_2 amount is low suggesting potential degradation to lactide. [27] The PiPOx-Tar shows the lowest thermal stability which is also in accordance with the hydrolysis stability. [15]

4. Conclusions

PiPOx networks crosslinked with various amino and hydroxy acids were synthesized, and their thermal properties, and thermal decomposition mechanism, were thoroughly investigated using thermogravimetric analysis complemented with mass spectrometry and DSC. The study demonstrated that crosslinking significantly enhances the thermal stability of PiPOx xerogels compared to the uncrosslinked polymer. The thermal stability of the xerogels was influenced by the chemical nature of the crosslinker, with amino acid type crosslinkers exhibiting slightly lower thermal stability compared to the PiPOx-Suc control xerogel due to the presence of charged amino groups, which can promote early thermal degradation. Moreover, the presence of hydroxyl groups within the crosslinker structure facilitates secondary reactions, leading to higher char residues. The DSC analysis revealed that the xerogels do not exhibit detectable T_g. However, all xerogels except PiPOx-Cys showed a broad exothermic transition above 220 °C, indicating structural or chemical rearrangements. These transitions may result from either polymer chain reorganization possible driven by hydrogen bonding or from crosslinking reactions involving unreacted functional groups. The thermal decomposition process was monitored using mass spectrometry, which revealed distinct degradation pathways depending on the chemical structure and number of functional groups found in the crosslinker. Notably, PiPOx-Tar xerogels exhibited decomposition primarily via depolymerization, likely due to the instability of the tartrate bond. In contrast, other xerogels degraded in a manner where the polymer backbone and crosslinks decomposed at similar rates, leading to a more uniform breakdown.

Overall, these findings suggest that PiPOx based xerogels have good thermal stability, making them suitable for high-temperature sterilization methods commonly employed in medical applications.

Acknowledgement

The authors acknowledge the Romanian Ministry of Research, Innovation and Digitalization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-

PED-2021-2544 within PNCDI III for the financial support. E.G. acknowledges the European Social Fund from the Sectoral Operational Program Human Capital 2014-2020, through the Financial Agreement with the title "Training of PhD students and postdoctoral researchers in order to acquire applied research skills - SMART", Contract no. 13530/16.06.2022 - SMIS code: 153734 for the financial support.

REFERENCES

[1] *E. Caló, V.V. Khutoryanskiy*, Biomedical applications of hydrogels: A review of patents and commercial products, Eur. Polym. J., Vol. **65**, Iss., 2015, p. 252-267.
[2] *M.F. Akhtar, M. Hanif, N.M. Ranjha*, Methods of synthesis of hydrogels ... A review, Saudi Pharm. J., Vol. **24**, Iss. 5, 2016, p. 554-559.
[3] *J. Zhu, R.E. Marchant*, Design properties of hydrogel tissue-engineering scaffolds, Expert Rev. Med. Devices, Vol. **8**, Iss. 5, 2011, p. 607-626.
[4] *L. Hanykova, J. Stastna, I. Krakovsky*, Responsive acrylamide-based hydrogels: Advances in interpenetrating polymer structures, Gels, Vol. **10**, Iss. 7, 2024, p. 414.
[5] *M. Teodorescu, M. Bercea*, Poly(vinylpyrrolidone) – a versatile polymer for biomedical and beyond medical applications, Polym. Plast. Technol. Eng., Vol. **54**, Iss. 9, 2015, p. 923-943.
[6] *M. Zare, A. Bigham, M. Zare, H. Luo, E. Rezvani Ghomi, S. Ramakrishna*, Phema: An overview for biomedical applications, Int. J. Mol. Sci., Vol. **22**, Iss. 12, 2021, p. 6376.
[7] *Z. Wang, Q. Ye, S. Yu, B. Akhavan*, Poly ethylene glycol (peg)-based hydrogels for drug delivery in cancer therapy: A comprehensive review, Adv. Healthc. Mat., Vol. **12**, Iss. 18, 2023, p. e2300105.
[8] *M. Bercea*, Recent advances in poly(vinyl alcohol)-based hydrogels, Polymers (Basel), Vol. **16**, Iss. 14, 2024, p. 2021.
[9] *S. Nemati Mahand, S. Aliakbarzadeh, A. Moghaddam, A. Salehi Moghaddam, B. Kruppke, M. Nasrollahzadeh, H.A. Khonakdar*, Polyoxazoline: A review article from polymerization to smart behaviors and biomedical applications, Eur. Polym. J., Vol. **178**, Iss., 2022, p. 111484.
[10] *B. Kopka, B. Kost, M. Basko*, Poly(2-isopropenyl-2-oxazoline) as a reactive polymer for materials development, Polym. Chem., Vol. **13**, Iss. 33, 2022, p. 4736-4746.
[11] *J. Kronek, A. Minarčíková, Z. Kroneková, M. Majerčíková, P. Strasser, I. Teasdale*, Poly(2-isopropenyl-2-oxazoline) as a versatile functional polymer for biomedical applications, Polymers, Vol. **16**, Iss. 12, 2024, p. 1708.
[12] *F.A. Jerca, V.V. Jerca, R. Hoogenboom*, Well-defined thermoresponsive polymethacrylamide copolymers with ester pendent groups through one-pot statistical postpolymerization modification of poly(2-isopropenyl-2-oxazoline) with multiple carboxylic acids, J. Polym. Sci., Part A: Polym. Chem., Vol. **57**, Iss. 3, 2019, p. 360-366.
[13] *F.A. Jerca, C. Muntean, K. Remaut, V.V. Jerca, K. Raemdonck, R. Hoogenboom*, Cationic amino-acid functionalized polymethacrylamide vectors for sirna transfection based on modification of poly(2-isopropenyl-2-oxazoline), J. Controlled Release, Vol. **364**, Iss., 2023, p. 687-699.
[14] *Z. Kronekova, M. Majercikova, E. Paulovicova, A. Minarcikova, M. Danko, J. Markus, S. Letasiova, J. Kronek*, Cytotoxicity and bioimmunological activity of poly(2-isopropenyl-2-oxazoline) conjugates with ibuprofen using 3d reconstructed tissue models, Biomacromolecules, Vol. **25**, Iss. 6, 2024, p. 3288-3301.

[15] *E. Ghibu, V. Vasile, I. Caraş, E.D. Giol, N.D. Banu, D.M. Vuluga, R. Stan, V.V. Jerca, F.A. Jerca*, Poly(2-isopropenyl-2-oxazoline) hydrogels with biodegradable junction points for drug-delivery applications, Chem. Mater., Vol. **36**, Iss. 15, 2024, p. 7459-7475.
[16] *B. Kopka, B. Kost, A. Pawlak, A. Tomaszewska, A. Krupa, M. Basko*, Covalent segmented polymer networks composed of poly(2-isopropenyl-2-oxazoline) and selected aliphatic polyesters: Designing biocompatible amphiphilic materials containing degradable blocks, Soft Matter, Vol. **19**, Iss. 36, 2023, p. 6987-6999.
[17] *R. Merckx, J. Becelaere, E. Schoolaert, O. Frateur, M.N. Leiske, D. Peeters, F.A. Jerca, V.V. Jerca, K. De Clerck, R. Hoogenboom*, Poly(2-isoproprenyl-2-oxazoline)-based reactive hydrophilic cross-linked nanofiber networks as the basis for colorimetric continuous meat freshness monitoring sensors, Chem. Mater., Vol. **35**, Iss. 17, 2023, p. 7079-7093.
[18] *V.V. Jerca, F.A. Nicolescu, R. Trusca, E. Vasile, A. Baran, D.F. Anghel, D.S. Vasilescu, D.M. Vuluga*, Oxazoline-functional polymer particles graft with azo-dye, React. Funct. Polym., Vol. **71**, Iss. 4, 2011, p. 373-379.
[19] *F.A. Jerca, V.V. Jerca, A.M. Anghelache, D.M. Vuluga, R. Hoogenboom*, Poly(2-isopropenyl-2-oxazoline) as a versatile platform towards thermoresponsive copolymers, Polym. Chem., Vol. **9**, Iss. 25, 2018, p. 3473-3478.
[20] *V.V. Jerca, F.A. Nicolescu, A. Baran, D.F. Anghel, D.S. Vasilescu, D.M. Vuluga*, Synthesis and characterization of side-chain oxazoline–methyl methacrylate copolymers bearing azo-dye, React. Funct. Polym., Vol. **70**, Iss. 10, 2010, p. 827-835.
[21] *H. Feng, M. Changez, K. Hong, J.W. Mays, N.-G. Kang*, 2-isopropenyl-2-oxazoline: Well-defined homopolymers and block copolymers via living anionic polymerization, Macromolecules, Vol. **50**, Iss. 1, 2017, p. 54-62.
[22] *F.A. Jerca, V.V. Jerca, R. Hoogenboom*, In vitro assessment of the hydrolytic stability of poly(2-isopropenyl-2-oxazoline), Biomacromolecules, Vol. **22**, Iss. 12, 2021, p. 5020-5032.
[23] *N. Tudorachi, A.P. Chiriac*, Tga/ftir/ms study on thermal decomposition of poly(succinimide) and sodium poly(aspartate), Polym. Test., Vol. **30**, Iss. 4, 2011, p. 397-407.
[24] *I.M. Weiss, C. Muth, R. Drumm, H.O.K. Kirchner*, Thermal decomposition of the amino acids glycine, cysteine, aspartic acid, asparagine, glutamic acid, glutamine, arginine and histidine, BMC Biophys., Vol. **11**, Iss., 2018, p. 2.
[25] *J.A. Portilla-Arias, M. Garcia-Alvarez, A. Martinez de Ilarduya, E. Holler, S. Munoz-Guerra*, Thermal decomposition of fungal poly(beta,l-malic acid) and poly(beta,l-malate)s, Biomacromolecules, Vol. **7**, Iss. 11, 2006, p. 3283-3290.
[26] *J. Telegdi, L. Trif, J. Mihály, E. Nagy, L. Nyikos*, Controlled synthesis and characterization of biodegradable, stereomer co-polycondensates of l-malic acid, J. Therm. Anal. Calorim., Vol. **121**, Iss. 2, 2015, p. 663-673.
[27] *F.D. Chattaway, F.E. Ray*, II. - The decomposition of tartaric acid by heat, J. Chem. Soc., Trans., Vol. **119**, Iss. 0, 1921, p. 34-37.