Evaluation of degradation of furanic polyamides synthesized with different solvents

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Abstract

Aromatic polyamides have properties of industrial relevance. However, the industrial and technological advancement has followed the trend of sustainability by seeking renewable source materials. In this work, polyamides were synthetized using 2,5-furandicarboxylic acid with p-phenylene diamine, triphenyl phosphite and two solvents (NMP and DMAc). To evaluate the influence of solvents on the reaction, a kinetic study of degradation was carried out by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and viscometric analysis. The viscosity value was in the range 70-80 mL/g. The TGA showed a higher thermal stability and activation energy for sample prepared with DMAc than the NMP. The XRD analysis showed that the PAF_{DMAc} presents more defined crystalline forms due to its higher solvation capability. The crystalline form can be correlated with the differences of Ea, because the crystalline orientation and the number of hydrogens bonds in sample PAF_{NMP} may be lower than the structure attributed to PAF_{DMAc}.

Keywords: *furanic polyamides, solvents, synthesis, kinetic degradation, crystallinity.*

1. Introduction

Aromatic polyamides are materials that exhibit an exceptionally rigid molecular structure characterized by high melting temperatures, low flammability, excellent tensile and impact strengths and differential thermal stability[1,2]. These properties are particularly manifested when all of the aromatic groups are linked in the para position[3]. Commercial aramids, mostly in the form of fibers, are used as reinforcement for thermal and ballistic protection[4].

With the foreseeable depletion of fossil resources, the rising price of raw materials, as well as environmental problems resulting from CO_2 emissions, there is increasing interest in the development of technologies for the utilization of renewable biomass[5]. The main power source originates from vegetal biomass, such as cellulose, glucose and fructose, which can be converted to compounds derived from furan[6-8]. The 5-hydroxymethylfurfural (HMF) is one of the most promising furan derivatives for the chemical industry because it is a starting point in the production of other furan compounds used in industrial applications[9], such as 2,5-furandicarboxylic acid (FDCA). FDCA has great potential as a monomer in the synthesis of polyamides from direct polycondensation of the components in the presence of phosphorous-containing derivatives[10]. The direct polycondensation method produces the best results in terms of structural regularity, high molecular weight and high thermal stability[11,12].

According to Odian[13], during the polycondensation process, the solvents utilized can affect the polymerization rates and the molecular weights as a result of preferential solvation of the reactants. Polar solvents enhance the rate of a polymerization because the transition state is more polar than the reactants. Therefore, the progress of a polymerization can be dramatically affected by specific interactions of a solvent with the functional groups of the reactants. The reactivity of a functional group can be altered by specific interactions with the solvent[13]. Results have shown that the best system for the polymerization of solvation have positive effects on the study of the kinetics of polyamide degradation. According to Gu et al.[14], the investigation of the kinetics and the mechanism of thermal degradation of new semi-aromatic polyamides containing a benzoxazole unit (BO_6) must be fully understood for its successful use in manufacturing and elevated temperature applications. Thermogravimetric analysis (TGA) has been widely used to determine the kinetic parameters of the degradation process, such as activation energy (E_A) using the Flynn-Wall-Ozawa (FWO) method[15,16]. The present study aims to evaluate the relationship between the thermal stability and the crystallinity of furanic polyamides synthesized with different solvents.

2. Materials

Triphenyl phosphite (TPP) was purchased from Aldrich Co. Ltd. (Milwaukee, Wisconsin, US), 2,5-furandicarboxylic acid (FDCA) was purchased from Satachem Co. Ltd. (Minhang Shanghai, China) and dried under vacuum at

80 °C for 8 h, *p*-phenylene diamine (PPD) was purchased from Acros Organics (Geel, Belgium) and used without further purification. N-methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc) were purchased from Vetec Ltd. (Duque de Caxias, Rio de Janeiro, Brazil) and purified by distillation at reduced pressure. Lithium chloride was purchased from Vetec Ltd. (Duque de Caxias, Rio de Janeiro, Brazil) and dried under vacuum at 100 °C for 8 h. The ethanol was purchased from Synth (Diadema, São Paulo, Brazil).

3. Methods

3.1 Synthesis of furanic polyamide

For the synthesis of furanic polyamide, 3.12 g (20 mmol) of FDCA, 2.16 g (20 mmol) of PPD and 1.2 g of LiCl were dissolved in 30.00 mL of NMP or DMAc. An aliquot of 12.00 mL (44 mmol) of TPP was pipetted into the solution to promote the condensation of the reaction. The reactants were mixed in a 250 mL glass reactor under mechanical stirring (300 rpm). The reaction was conducted under nitrogen to create an inert atmosphere and heated to 130 °C for 8 h. After 1 h, reduced pressure was applied to force the withdrawal of the water formed during the reaction[17].

After completion of the reaction, and the system returned to room temperature, the sample was poured into a beaker with ethanol for washing, forming a precipitate that was subsequently filtered under reduced pressure in a Buchner funnel coupled to a Kitasato flask. Finally, the sample was dried in a vacuum oven at 80 °C for 24 h. The conversion of the synthesized polyamides was approximately 90%. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ (ppm) 10.55 (s, 1H - hydroxyl), 7.94 (s, 1H - amide), 7.85 (s, 1H - furane), 7.79 (s, 1H - furane), 7.71 (d, 1H - benzene), 7.66 (dd, 1H - benzene), 7.60 (d, 1H - benzene), 7.52-7.36 (m, 1H - benzene), 3.66 (s, 2H - amine).

3.2 Intrinsic viscosity

The viscosities of polyamides were determined from solutions with concentration between 0.0005 and 0.003 g.mL^{-1} in sulfuric acid 98% at 30 ± 0.1 °C. The viscometer used was the Cannon-Fenske n° 520 20, capillary 1.01 mm. The results were obtained by graphical extrapolation using the *Huggins* equation (η$_{red.}$ *vs* C).

3.3 X-ray diffraction

X-ray diffractograms (XRD) were collected in powder form with monochromatic CuKa radiation (λ = 0.15418 nm) using a sample holder mounted on a Siemens D500. Intensities were measured in the range of 5° < 2θ < 50°, typically with scan steps of 0.05° and 2s step^{-1} (1.5min^{-1}).
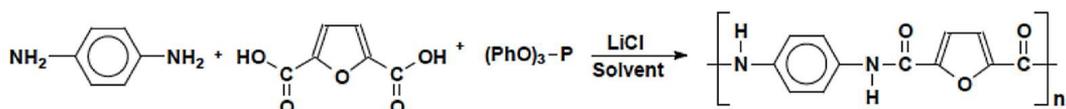
3.4 Thermogravimetric analysis

The TGA analyses were performed on a Q50 (TA Instruments) under an atmosphere of N$_2$ (40 mLmin^{-1}) at different heating rates (5, 10, 20, and 40 °C.min^{-1}). The mass used for the analyses was 10mg. These results were used to estimate the kinetic parameters of degradation. The apparent activation energy (E_A) of degradation was determined using the Flynn-Wall-Ozawa (FWO) method. The FWO is an isoconversional method and is described by the Equation 1.

$$\ln \beta = \ln \frac{AE_a}{g(\alpha(T))R} - 5.330 - 1.052 \frac{E_a}{RT} \qquad (1)$$

Where $g(\alpha(T))$ is a function of the degradation process, E_A is the activation energy, R is the gas constant, A is the pre-exponential factor, $β$ is the heating rate and T is the temperature. According to this method, the rate of reaction is dependent only of the temperature. Considering the temperature dependence, isolating the *log β* vs *T* for different heating rates a linear behavior can be observed and the E_A can be obtained by the angular coefficient of the strain line[15,16,18]. The estimation of the E_A values and the statistical error of the fits were determined according the ASTM E 1641–07 and ASTM E 698 – 05.

4. Results and Discussions

4.1 Polymer synthesis

In the polycondensation of polyamides, the phosphite group is employed as a condensing agent, which is consumed over the course of the reaction because it is the main agent responsible for the conversion. For each mole of the amine group to react, one mole of the phosphite group[19] must be present. The addition of the inorganic salts increases both the solubility of the polymers in the average reaction and their viscosity, which consequently leads to higher yields and molecular weights of the polyamides. Scheme 1 illustrates the general reaction pathway for this synthesis.

During the polycondensation process, a polar aprotic solvent is added to solubilize the part of the non-polar chain, whereas inorganic salts, such as LiCl, are used to interact with the polar portion, increasing the solubility of the polymer in the solution and diminishing the strength of the interchain hydrogen bonds. Solvents that have been proven effective for this method are N-methylamides, particularly NMP and DMAc. The progress of the reaction was followed by the evolution of the polymer yield and the intrinsic viscosity in the determined reaction time.

The intrinsic viscosity can be attributed to the hydrodynamic volume by the interaction of hydrogen bonds associated with increased symmetry and efficient packing of the polymer chains[20]. The viscosities of PAF$_{DMAc}$ and PAF$_{NMP}$ were estimated at 74 and 77 mL/g, respectively. This is a

Scheme 1. Synthesis of polyamides using triphenyl phosphite (TPP).

factor that is directly related to the molecular weight of the aromatic polyamides.

The solvents in this reaction were added in order to determine the best synthesis conditions. The choice of solvent is important because of the solubility of the polymer during the reaction favors the polycondensation.

From this evaluation, it is clear that the progress of the polymerization can be directly affected by specific interactions of the solvent with the functional groups of the reactants, ie, the reactivity of the functional group may be modified by the interaction with the solvent[13]. In order to understand the importance of solvation on the final result, a polymerization was carried out to study the degradation kinetics of furânicas polyamides in order to check the relationship between the thermal stability of microstructure and polyamides.

4.2 Degradation behavior

Polyamides were characterized in relation to their thermal properties. These properties are directly associated with the intermolecular forces of the chains and the molecular weight of the polymer. Strong intermolecular interactions increase the thermal stability of the polyamide, facilitating packing of the polymer chains. The higher packaging causes high rigidity of the chains which prevent their mobility, hindering from obtaining a glass transition temperature and consequently determination of the degree of crystallinity due to its structural characteristics.

Figure 1 shows the thermogravimetric analysis. Three degradation stages were observed in the range of 50-100°C, 150-250°C and 300-600°C, respectively. The first range is associated with the solvent or water residues because of the higher concentration of hydrogen bond, *e.g.*, among the amide and H_2O groups. The second range of degradation may be correlated with the monomers that did not reacted, forming dimers and trimers. The third range of degradation is principally associated with the polymer backbone[21]. For the polyamide synthesized using NMP the percentage of polymer degraded in the third range was 33% and for the use of DMAc was 28% of weight. The residual mass was 60% and 33% to PAF_{DMAc} and PAF_{NMP} samples, respectively. The percentage of polymer maybe not correlated with the conversion of polymer in the synthesis because the thermogravimetric curves are a sum of physical and chemical phenomena, which occur randomly. However, the difference observed between the temperature ranges of the third degradation phenomena suggests that the solvents used cause differences in the microstructure of the polyamides, *e.g.*, molecular packing. Moreover, the XRD analysis showed differences in the crystal formation. Just as Kevlar, the furanic polyamide does not present a precise melting point and because of this the temperature is higher and the degradation is difficulted by differences in the crystal formation.

Figure 2 illustrates the third range of degradation (300-600°C) at 5, 10, 20 and 40 °Cmin⁻¹. This range of degradation was selected to study because it represents the chain backbone. The progress of the degradation reaction (α) is determined only in this region and the α values between 0 - 1 correspond to this range degradation. The increase in the heating rate shifts the degradation to higher temperatures. This linear shift allows application of the kinetic methods

such as the isoconversional method of Flynn-Wall-Ozawa (FWO)[18]. Figure 3 shows the linear fit by the FWO method. The range of linear fit is between α = 0.05 – 0.8. The linear fits are determined with a confidence interval of 95% and the correlation coefficients (r) were, for all fits, between 0.9985 – 0.1000. E_A is obtained by the slope of the straight line of the fit (slope=E_A/R) and the results are showed in Figure 4.
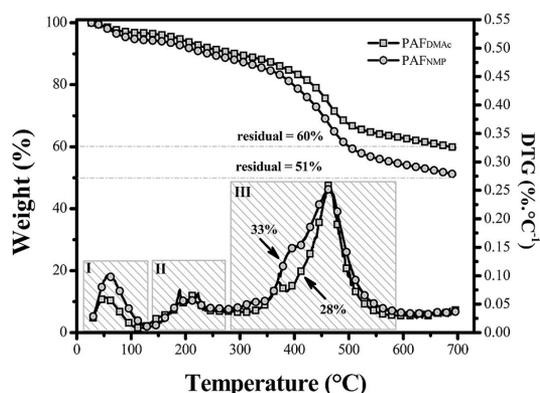

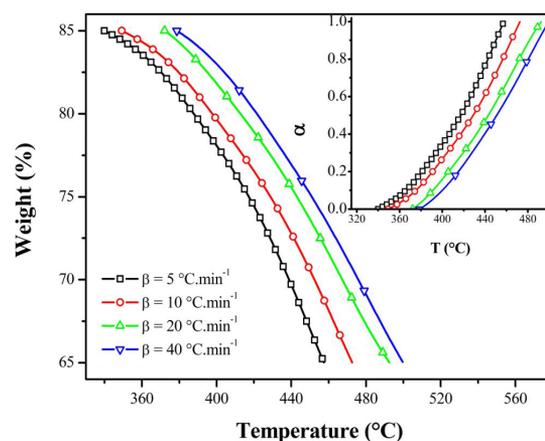**Figure 1.** TGA analysis obtained for the PAF studied (β =10°C min⁻¹).

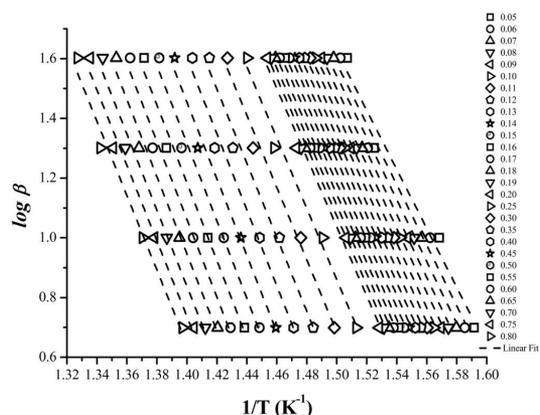**Figure 2.** TGA analysis obtained to the PAF_{DMAc} sample at different heating rates.

Figure 3. FWO fits obtained to the PAF_{DMAc} sample.

Through the temperature range of 300 – 600 °C used to determining E_A were observed values between 178 – 238 kJmol^{-1} and 301 – 357 kJmol^{-1} for PAF$_{NMP}$ and PAF$_{DMAc}$ samples, respectively. For some PA studied, in the literature the E_A shows values next to the obtained with NMP. For example, Herrera et al.[22] showed values of 162, 91 and 164 kJmol^{-1} to PA6, PA66 and PA612, respectively (values

in the range between 250-475 °C). Gu et al.[14] obtained a E_A of 197 kJmol^{-1} for a semi-aromatic polyamide containing benzoxazole at ≈ 425°C and Amintowlieh et al.[23] obtained 201 kJmol^{-1} for a PA6 at 437 °C. These values are expected for non-aromatic PA and the variations among them are due to the variation of the crystalline degree and the concentration of amide groups per repetitive unit. Expected values for an aromatic polyamide such as Kevlar are in the range 300 kJmol^{-1} and 200 kJmol^{-1} under dry nitrogen and air atmospheres, respectively[24]. The differences of E_A may be due to the crystal orientation and the number of hydrogen bonds present in the microstructure of each polyamide, which could be less for use of NMP because more difficulty on its solvation effect.
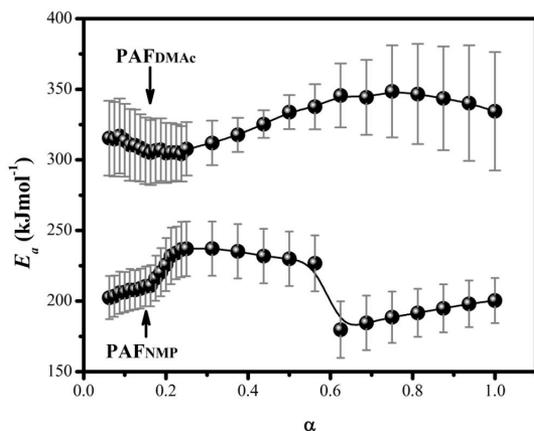
4.3 Crystallinity characterization

The crystallinity of the aromatic polyamides, shown in Figure 5, can be evaluated by measurements of X-ray diffraction in the range of $2\theta = 20$ to $35°$, showing, in most cases, two diffraction peaks attributed to crystallographic planes (200) and (110). These peaks are described as the carbonaceous interlayer[25]. The value of 2θ of the plane (200) is related to the distance between adjacent layers which interact primarily by van der Waals forces and to some extent by π-electron overlap. The value of 2θ at the crystal plane (110) is, however, related to the distance between adjacent polymer chains along the crystallographic (110), (110), (110) and (110) planes, which are characterized by an evident concentration of intermolecular interactions[26].

The PAF$_{DMAc}$ exhibits two diffraction peaks at $2\theta \approx 23°$ and $24°$ attributed to the (200) and (110) diffraction planes, respectively, indicating a semi crystalline form using solvent DMAc. The narrow diffraction peaks suggest a more ordered crystalline form. This XRD pattern indicates the presence of a semi crystalline state that formed during the polycondensation[27].

PAF$_{NMP}$ showed a broad halo at approximately $2\theta \approx 25°$, indicating an amorphous polymer, which is most likely a result of the less organized structure caused by poor solvation. This amorphous form suggested by the wider diffraction peaks[28] could be explained by the decrease of intermolecular forces of the aromatic polyamides[29], promoting distortion of the polymer chain, hindering regular chain packing.

Figure 6 illustrates the probable structure of PAF$_{NMP}$, suggesting less interaction between the layers compared

Figure 4. Evolution of the E_A in the third stage of degradation correlated with the backbone chains of the PAF.

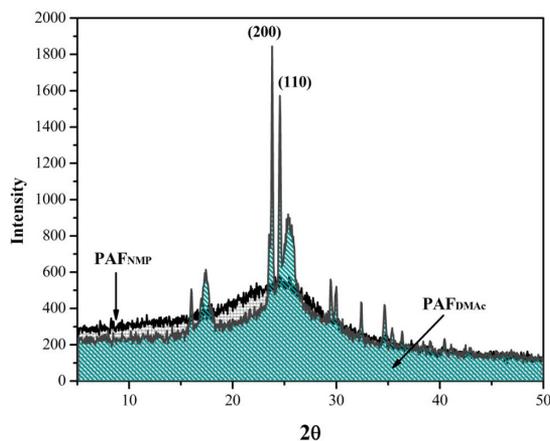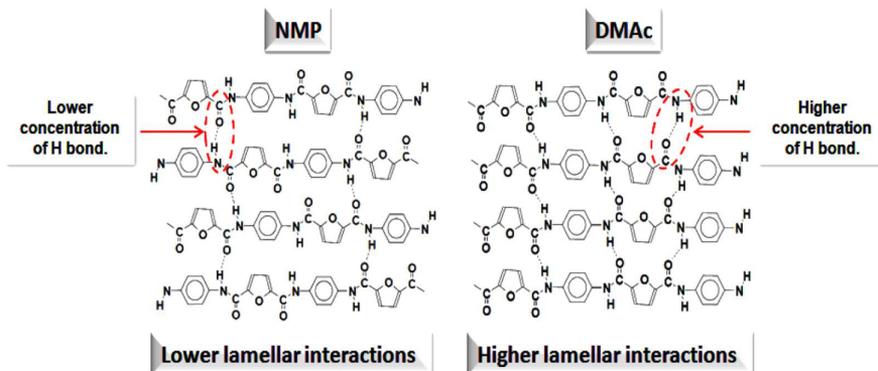**Figure 5.** X-ray diffraction diagram of the polymers.

Figure 6. Draw illustrates of the lamellar orientation correlated with the polyamides with the different solvents.

to the structure attributed to PAF$_{DMAc}$. In this case, greater lamellar interaction is formed because of the larger number of hydrogen bonds. The behavior of these structures may also be related to the crystallinity of the polyamides as well as the XRD analyses presented.

PAF$_{DMAc}$ exhibits more defined crystalline forms because of the higher solvation power of DMAc[30]. The interaction forces between the polyamide chains also increase the interactions between the lamellae, facilitating the formation of hydrogen bonds between the carbonyl and amine groups, and the forces involved in aromatic stacking.

The reactivity of the functional group can be altered by specific interaction with the solvent. These results have shown that better solvating systems have an effect on the degradation of polyamides. Thus, the more defined crystalline forms suggest that the use of DMAc as solvent may be favorable because of its greater degree of freedom and its less steric hindrance compared to the NMP solvent, allowing a greater packaging of the polymer during the synthesis, as well as better thermal properties. The influence of the solvent is given by the dielectric constant of 38.85 for DMAc compared to 32.55 for NMP, facilitating the solvation of the system and subsequently increasing the crystal formation in the chain[31,32].

5. Conclusions

Furanic polyamides were synthesized using 2,5-furandicarboxylic acid (FDCA) obtained by the oxidation of HMF (hydroxymethylfurfural) with p-phenylene diamine (PPD) and triphenyl phosphite (TPP). Two different solvents, NMP (N-methyl-2-pyrrolidone) and DMAc (N,N-dimethylacetamide), were employed to evaluate the solvation effect on the resulting microstructures and degradation characteristics. The TGA analysis showed higher thermal stability for the PAF synthesized with DMAc than NMP suggests that the solvents used cause differences in the microstructure of the polyamides. The activation energy was higher using DMAc corroborating the higher thermal stability. The XRD analysis showed higher ordered crystalline structure to the PAF$_{DMAc}$ than PAF$_{NMP}$ and this difference was attributed to the concentration of hydrogen bonds between layers. The more defined crystalline forms suggest that the use of DMAc as a solvent may be favorable because of its higher degree of freedom and lower steric hindrance compared to NMP, allowing for greater packing of the polymer during the synthesis.

6. Acknowledgements

7. References

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