Mechanochemical Production of Urea-citric Acid Copolymer

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Abstract. Increasing non-biodegradable plastic consumption is a great factor that contributes to worldwide pollution and global warming. Mechanochemistry provides a clean, solvent-less, route for chemical reactions such as polymerization based on the absorption of mechanical energy. Urea polymers have several applications in industrial and medical area, such as paints, resins, plastic, wood glue, separating aliphatic hydrocarbons, coating, and pharmaceutical drugs. In this study, a copolymer of urea and citric acid was synthesized using a planetary ball mill as grinder with fixed reaction time and rotational speed, varying the number and material of the planetary ball mill sphere to find the effects of those two conditions in the yield percentage of the copolymer. The purified polymer was characterized by Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance – NMR. Results confirmed that polymeric material is formed by the reaction between citric acid and urea without any catalyzer using mechanochemistry. NMR results showed that the reaction occurred between urea and the acid groups at the ends of the chain, while the central COOH remained intact.

1. Introduction

Generally, polymerization reactions are carried out in reactor in the presence of organic solvent medium. That fact creates many problems such as solvent loss, need to recover and recycle solvents, and contamination of solvent in the polymeric material. Different polymerization techniques were developed to obtain polymers without the use of organic solvent, like supercritical polymerization and mechanochemical reaction. The mechanochemistry's goal is to transform energy from mechanical forces to promote interaction between chemical structures. That energy can be provided to the different set of mechanical actions such as impact, compression, shearing and grinding [1]. So, a mechanical activation technique allows to perform the polymeric synthesis without organic solvents [2]. Besides, mechanochemical reactions provide excellent control of the reaction stoichiometry [3] and higher reaction rates due to absence of solvents [4]. In this context, the following work aims to produce urea...
and citric acid copolymers via mechanochemical synthesis and characterize the polymeric material by infrared spectroscopy and Nuclear Magnetic Resonance – NMR.

2. Experimental

Materials

All reagents and solvents were purchased as analytical grades from their respective suppliers and used as received. Urea ((NH2)2CO), M.M. = 60.07 g/mol, 99.5% minimum purity, supplied in the form of small granules by Petróleo Brasileiro S.A. Citric acid (C6H8O7) M.M. = 192.124 g/mol, purity > 99% supplied as small grains by Merck Comércio Importação LTDA. All the reactants were previously analyzed via FTIR (Fourier-transform infrared spectroscopy) to assure their purity.

Methods

Mechanochemistry synthesis. For the experiments, Adventurer® Precision Electronic Balance, AR2140BR - OHAUS with precision of 0.001g and a Retsch model PM-100 Planetary Ball Mill were used. Briefly, urea and citric acid were weighted, approximately 10 g of total mass, following a molar ratio of 1:1 [5]. After that, the monomers were transferred to stainless steel, agate and tungsten carbide vessels (50 cm3), which were loaded with balls 10 mm in diameter. The system was milled separately in the mill without solvent, as suggested by Landim et al. (2017) [6]. Reaction conditions were fixed in 550 rpm rotational speed, 60 minutes to polymerization reaction (with 1 minute pause every 5 minutes), applying direction reversal on each break as suggested by Landim (2018) [7].

Product purification (Filtration and Drying). The product purification (after synthesis) was performed by vacuum filtration using ethanol as wash solvent. Ethanolic solution was dried in a rotary evaporator (IKA HB10) with bath previously heated until 50 ºC under stirring (80 rpm) in order to determine the residual content. After purification, the resulting polymer was dried in an oven (Quimis’ 0317M-42) at 65 ºC for 6 hours. After that, polymeric material was led to a silica-filled glass vacuum desiccator for 30 minutes until room temperature was achieved.

Reaction Yield. The yield of the copolymer synthesis was calculated through Equation 1, where n is the yield in percentage, m1 is the copolymer weight and m2 is initial reactant mass.

\[ n\% = \frac{m_1 \times 100}{m_2}, \]

Infrared spectroscopy (FTIR). Infrared spectroscopy analysis was performed by Shimadzu FT-IR IRAfinity-1 equipped in an ATR device with a Germanium-coated KBr beam splitter and a DLATGS detector in the wavelength region of 4000-400 cm⁻¹ with a precision of 4 cm⁻¹ to observe the polycondensation/esterification process and to estimate the extent of the reaction. An average of 128 scans was recorded.

3. Results

Variables X Polymer Yield

In this study, fixed values of time (1h) and rotation (550 rpm) were adopted. The studied variables were the number of spheres and the type of material of the spheres, and the response variable was the reaction yield. 10 reaction runs were carried out in duplicate (Table 1). The highest yields were obtained with 02 spheres. In this way, the number of spheres was fixed at 02, and the type of material used was varied, to evaluate the influence of the composition of the material on the reaction yield.
Table 1. Effect of the number of spheres on the mechanosynthesis of the UAC copolymer

| Run | Spheres | Yield (%) |
|-----|---------|-----------|
| 1   | 1       | 77        |
| 2   | 1       | 74        |
| 3   | 2       | 82        |
| 4   | 2       | 79        |
| 5   | 4       | 71        |
| 6   | 4       | 68        |
| 7   | 6       | 77        |
| 8   | 6       | 74        |
| 9   | 2       | 80        |
| 10  | 2       | 78        |

Table 2. Influence of material composition on polymer yield

| Constitution of the reactor and spheres | Yield (%) |
|----------------------------------------|-----------|
| Stainless Steel                        | 82        |
| Tungsten Carbide                       | 70        |
| Agate                                  | 52        |

Three different materials were evaluated, stainless steel, tungsten carbide and agate. And the best yields were obtained with stainless steel. Table 2 shows the yield values obtained by varying the type of material used. As the density of stainless steel is higher, it was expected a higher yield using this material, which was confirmed by the results presented in Table 2.

Concerning the IR analyses, it was expected to occur peaks in the regions of 3480 to 3200 cm⁻¹ and 1720 to 1650 cm⁻¹ for the urea, and 1750 to 1600 cm⁻¹ for acid citrus [5]. This was confirmed in the analyzes performed, which are shown in Figures 1. In this case, the N - H bands in the region of 3437 cm⁻¹ and 3360 cm⁻¹ were observed, and the presence of energy peaks in 1670 cm⁻¹ and 1634 cm⁻¹ which is a band characterized by the presence of urea carbonyl. As for citric acid, the characteristic peak was observed in the 1693 cm⁻¹ region that characterizes a carboxylic acid.

![Figure 1. Infrared of Urea (top), Citric Acid (middle) and Copolymer (bottom)](image-url)
The formation of amides in the region of 3841 cm⁻¹ and 3344 cm⁻¹ was verified for the polymer. The 1643 cm⁻¹ band suggests the presence of the carbonyl amide group (-NH-C = O) formed through reaction between citric acid and urea. The formation of amides attests that mechanochemistry is efficient in transforming mechanical energy into chemical energy necessary for the condensation reaction.

Figure 2. ¹H (left) and ¹³C (right) Nuclear Magnetic Resonance Spectra of copolymer in DMSO-d₆

The hydrogen and carbon nuclear magnetic resonance (NMR) spectra of the copolymer obtained are shown in Figures 2. In the ¹³C NMR the presence of five carbon atoms is observed, three of which refer to carbonyls (160.6 to 175.1 ppm) as well as the presence of two aliphatic carbons, one carbinolic at 72.9 ppm and the other at 39.8 ppm, corresponding to the citric acid portion. The two spectra correspond to the symmetrical unit of chemical formula below, whose signals reveal that the reaction occurred between urea and the acid groups at the ends of the chain. The carboxylic acid unit of the central part of the chain is also confirmed in the ¹H NMR spectrum where the presence of a hydrogen at 12.5 ppm is observed for one unit of hydrogen.

Based on the results, it is possible to claim that the polymer synthesis yield was 82% and the polymeric material is soluble in water but insoluble in ethanol. Thus, it was confirmed that the reactor is efficient in promoting polymeric synthesis, generating the polymer claimed by an easy-to-handle and environmental-friendly route.

References
[1] Tan, D.; Garcia, F. Main group mechanochemistry: From curiosity to established protocols. Chem. Soc. Rev. 2019, 48 2274-2292.
[2] Chaves, C.M.M. Novas Metodologias em química sustentável. Universidade de Coimbra. 2015.
[3] Schmidt-Naake, G.; Frendel, A.; Drache, M.; Janke, G. Chemical Engineering & Technology, 24 889 2001.
[4] Wang, G.W., Komatsu, K., Murata, Y., Shiro, M., 1997. Synthesis and X-ray structure of dumb-bell-shaped C120. Nature 387 583.
[5] Paleckiene, R.; Sviklas, A.; Slinksiene, R. Reaction of urea with citric acid. Russian journal of applied chemistry, 78 (10) 1651-1655, 2005.
[6] Landim, Lucas B. et al. Synthesis and characterization of copolymers of urea–succinic acid–ethylene glycol and copolymers of urea–succinic acid–glycerol. Polymer Engineering & Science, 58 (9) 1575-1582, 2017.
[7] Landim, Lucas B. et al. Synthesis and characterization of copolymers of urea–succinic acid–ethylene glycol and copolymers of urea–succinic acid–glycerol. Polymer Engineering & Science, 58 (9) 1575-1582, 2018.

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