PMMA Hydrolysis in Subcritical Water: temperature, time and pH effects

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1. Introduction

Poly(methyl methacrylate) (PMMA) is a synthetic and amorphous polymer that belongs to the acrylate family. It is an optically clear polymer with a glass transition temperature range of 100ºC to 130ºC; a density of 1.20 g/cm3 at room temperature and a melting point of 130ºC. It presents high resistance to sunshine exposure, high impact strength, high scratch and shatter resistance, good optical properties, good degree of compatibility with human tissue, is lightweight and exhibits favourable processing conditions and a reasonable resistance to chemicals[1] ~~[1].~~ Considering these properties, PMMA is widely used in architecture and construction, lighting, automotive and transportation, electronics, nanotechnology, medical and healthcare, and furniture. Very promising application have been developed with PMMA in the recent years through the polymer foaming with supercritical CO_2. The produced foams present very low thermal conductivity, which make them a great insulation material[2].

Although the foaming of PMMA with supercritical CO_2 can make good insulating material, there is still room to optimize the process. The main topics to improve are: increase of the cell density, drop of the cells size, make clear foams and very importantly, convert the production in an efficient, cost effective and continuous process. In this sense, the use of water has been proposed as an inert solvent to prevent PMMA agglomeration and facilitate its foaming. Despite its hydrophobic nature, PMMA can absorb ~2% w/w water and it was demonstrated that water absorption could produce swelling in this polymer[3] ~~[2]~~. Then, it becomes important to evaluate the stability of the polymer in the presence of water, at different temperatures and pH values.

This work studies hydrolysis of PMMA in different media (natural, acidic and alkaline). If the polymer hydrolyzes and changes its molecular weight, it is possible to obtain copolymers different in structure and properties[4] ~~[3]~~. PMMA can be hydrolyzed completely with sulfuric acid to become poly (methacrylic acid) (PMAA)[1] ~~[1]~~. However, isotactic and syndiotactic PMMAs were hydrolyzed in a different extent due to a mechanistic explanation[5] ~~[4]~~. Regarding alkaline hydrolysis, PMMA was not hydrolyzed at all at low temperatures (37ºC)[6] ~~[5]~~.

An alternative method for the hydrolysis reaction was reported using simple and readily available equipment found in all chemical laboratories, namely autoclave. The effects of temperature, time and the pH media on the hydrolysis of PMMA and the hydrolysed products have been analysed. Based on results, an optimum set of conditions for the hydrolysis reaction of a hydrophobic polymer will be proposed.

2. Materials and Methods

PMMA Plexiglas® 7N was supplied by EVONIK in the form of pellets. Sodium hydroxide pellets and sulfuric acid (72%) were purchased from Panreac and used to adjust the pH towards the alkaline and acidic media, respectively. All reactants were used as received without further purification.

About 11,9 ~~m~~g of polymer was placed in a 100-ml pressure tube and suspended in 40 ml of MiliQ water. For alkaline and acidic media, the same amount of PMMA was weighted with varying amounts of additive to reach the desired pH. The reaction mixtures were heated at two different temperatures (120 and 150ºC) using oil-bath for various periods of time (30, 60, 90 and 120 minutes).

After each cycle the resultant solution was allowed to cool down to room temperature. The supernatant was collected from the cooled reaction mixture by filtration and the pH was determined. Colour change was taken into account. The dissolved solids were measured to determine the level of hydrolysis at the different conditions. Also, the samples were subjected to the following analytical techniques: high performance liquid chromatography (HPLC) to determine the composition of the liquid products. Gel permeation chromatography was used to determine the molecular weight of the raw material. In order to identify the main functional groups, attenuated total reflection infrared (ATR-IR, Bruker Platinum ATR) spectroscopy was employed. The pH of the samples was measured with a Jenway Model 3505 pHmeter. Particle size distribution was measured by Mastersizer 2000 analyzer.

3. Results and discussion

It has been found that in natural media (conventional aqueous–hydrolysis) no water solubility of PMMA is achieved, although swelling of particles is observed at the highest temperature (150ºC) and as the time increased (≥ 60 min.). At this temperature, the polymer turned its transparency into opaque white form as shown in Fig. 1.

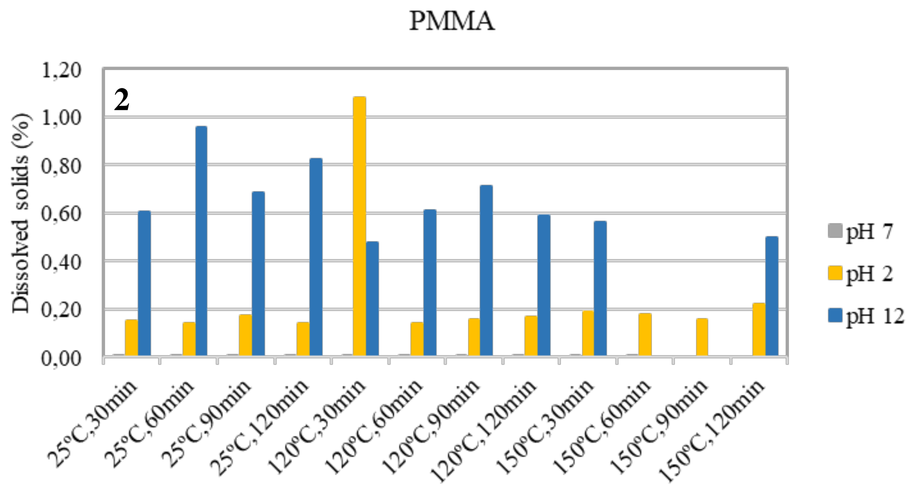

Figure 1. Products of alkaline hydrolysis of PMMA at 150ºC. Figure 2. PMMA hydrolysis at different conditions of dissolution media, temperature and time.

By this procedure, PMMA absorbs ≈11.60% of water. As shown in Fig. 2 it was clearly noticed that the amount of dissolved solids increases in the alkaline media in comparison with the acidic one. No significant results were achieved in the natural media.

4. Conclusions

It is worth emphasizing that degree of hydrolysis in the different media studied could depend on temperature. Further hydrolysis in acid and basic conditions, and different combinations of solvents will be conducted comparing with neutral media.

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