

Water Influence in Poly(epichlorohydrin) Synthesis: An Intermediate to Energetic Propellants

Jairo Sciamareli*¹, Silvana Navarro Cassu¹, Koshun Iha²

¹Instituto de Aeronáutica e Espaço - São José dos Campos/SP - Brazil

²Instituto Tecnológico da Aeronáutica - São José dos Campos/SP - Brazil

Abstract: Poly(epichlorohydrin) was synthesized using anhydrous and hydrate stannic chloride, separately, as initiator. Reactions were conducted in the presence of a diol at 70°C. Polymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and hydroxyl value determination. It was observed that water has influence in growing chain, but not in its structural backbone. Besides, the monomer/initiator relationship has a higher influence in overall poly(epichlorohydrin) properties.

Keywords: Synthesis, Poly(epichlorohydrin), Hydrate Initiators.

INTRODUCTION

Poly(epichlorohydrin) (PECH) has been used to prepare glycidyl azide polymer (GAP), a worthy energetic material that can be used alone or associated with other polymers in copolymers, as energetic binder, to improve mechanical and ballistics properties in rocket propellants (Eroglu and Guven, 1996; Frankel *et al.*, 1992; Mojan *et al.*, 2004; Sciamareli, 2009a). In a general way, better mechanical properties in propellants are obtained when the polymer has a molecular weight between 2000 and 3000g/mol and hydroxyl value is up to 1.0mmol/g.

Important GAP properties, as molecular weight, hydroxyl value and functionality, are obtained in PECH synthesis, since the molecular structure is preserved during the PECH to GAP transition (Sciamareli, 2009b).

Polymerization of epichlorohydrin (ECH) proceeds by cationic mechanism in presence of Lewis acid like boron trifluoride etherate and stannic chloride. Diols, such as butane diol, act as co-initiators or chain transfer agents. The resulting polymer has hydroxyl terminal groups (Biedron *et al.*, 1991; Francis *et al.*, 2003).

In this kind of experiment, water can act as an initiator in polymerization reaction and, further, as a deactivating agent, introducing the OH group at the end of the final product

(Biedron, 1991; Guanaes *et al.*, 2007; Okamoto, 1984; Qureshi and Ochel, 1996).

The aim of this work was to investigate the influence of water and monomer/initiator relationship in PECH synthesis. In these experiments, it was used, separately, anhydrous and hydrate initiator, respectively, SnCl₄ and SnCl₄.5H₂O, and their results were compared. The experimental procedure was the same and reagents were similar, with the exception of the initiator.

EXPERIMENTAL

Materials

ECH, 1,2 dichloroethane and trifluoroacetic acid (Sigma). Anhydrous stannic chloride (Riedel). Pentahydrate stannic chloride (Vetec), as well ethylenediaminetetracetic tetrasodium salt hydrate (EDTA tetrasodium) and acid hydrochloride. Ammonium hydroxide (J. T. Baker). All reagents were used as received, without treatment. Only 1,4 butanediol (Sigma) was treated with calcium sulphate before being purified by vacuum distillation.

Synthesis of PECH

Reaction of the ring-opening polymerization of ECH was carried out in a 300mL three-neck round bottom-flask,

Received: 21/12/11. Accepted: 06/01/12

*author for correspondence: jairojs@iae.cta.br/Pç. Mal. Eduardo Gomes, 50. CEP: 12.228-901 - São José dos Campos/SP - Brazil

containing a magnetic stir bar and a dropping funnel. 1,4 butanediol and 1,2 dichloroethane were stirred to obtain homogeneous solution. First, stannic chloride was introduced to round bottom-flask and, in sequence, trifluoroacetic acid was added. The system was warmed by an oil bath up to 70°C. ECH was added, drop by drop, using the dropping funnel at a rate of 30g per hour. When the ECH addition was finished, the system was warmed for another hour. The reaction was quenched by adding distilled water and acid hydrochloride. After being stirred for ten minutes, solution was transferred to a separatory funnel. Separated organic phase was stirred again with a water solution containing EDTA tetrasodium and ammonium hydroxide. One more time, resulted solution was transferred to a separatory funnel and, after being separated, organic phase was washed with distilled water. This last part was repeated for another four times. At last, polymer was obtained by removing the solvent by vacuum distillation.

Analysis of the polymers

FT-IR analyses were performed by PerkinElmer spectrophotometer, Spectrum 2000 in the spectral region of 4000 to 400 cm^{-1} , gain 1, resolution of 4 cm^{-1} and 40 scans. Samples were analyzed by transmission technique as liquid film. Gel permeation chromatography analyses were conducted by a PerkinElmer Series 200 equipped with NUCLEOGEL GPC 103-5 VA300/7.7 column, tetrahydrofuran was the mobile phase and it was calibrated with polystyrene standards. Thermal analyses were carried out in a DSC TA Instruments Q100, from -90 to 40°C, at 20°C/min heating rate, in nitrogen atmosphere, using 2-3mg of sample. CH analyses were recorded by a PerkinElmer 2100 II, at 925°C under oxygen and helium flow using 2-3mg of sample. OH analyses were made according to open literature (Dee *et al.*, 1980).

RESULTS AND DISCUSSION

This work was carried out with a monomer/initiator relationship of 20:1 and 60:1. Figure 1 compares FT-IR spectra obtained to 20:1 and Fig. 2 compares spectra to reaction with 60:1 relationship, where (A) is a spectrum relative to use $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and (B) is relative to use SnCl_4 anhydrous.

Spectra in Fig. 1 are very similar. Both present the characteristics PECH peaks at 3470-3442 cm^{-1} , 1119-1115 cm^{-1} and 749-747 cm^{-1} , corresponding to OH, C-O-C and CH_2Cl functional groups, respectively (Silverstein *et al.*, 1981).

Spectra in Fig. 2 are very similar too. In a general way, all the spectra show resemblance aspect. They present the same absorptions at the same position, in evidence that water does not up set structural backbone formation of PECH.

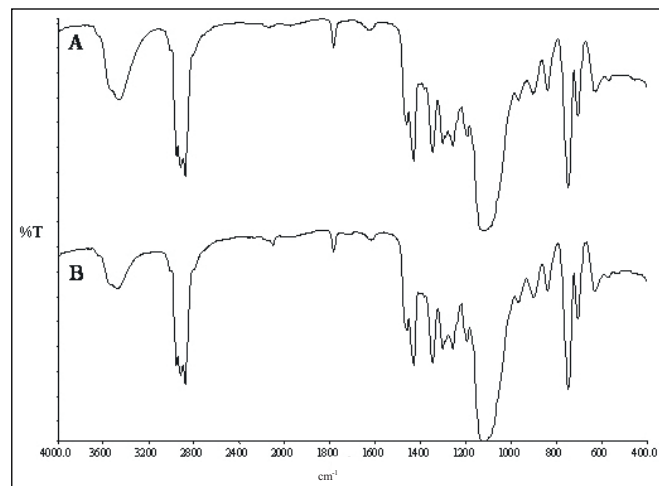


Figure 1. PECH spectra with monomer/initiator relationship of 20:1.

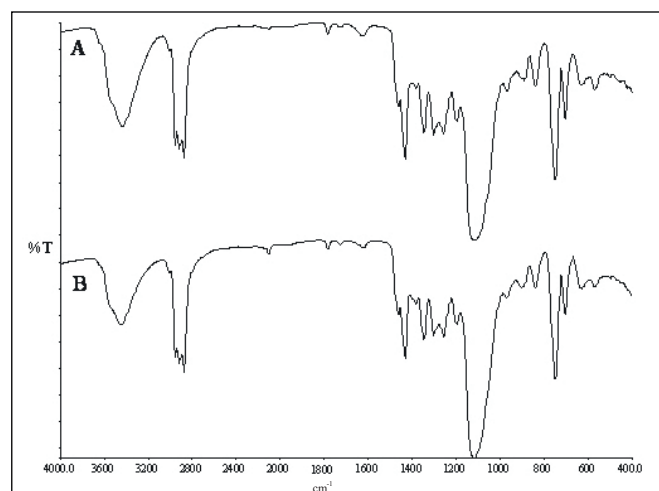


Figure 2. PECH spectra with monomer/initiator relationship of 60:1.

According to results in Table 1, when it is compared to the action of anhydrous and hydrate initiator, it is possible to realize a clearly tendency to higher molecular weight when anhydrous SnCl_4 is used. When it is compared to the quantity of the initiator, it is possible to observe that higher concentration of this reactant also carries out to higher molecular weight. This is reported elsewhere (Sciamareli, 2009b). Anyway, these results were expected, since it is known that water act as a chain end, avoiding their enlargement. To the same quantity of monomer, shorter chain means a higher number of chains with lower size. Furthermore, it shows the importance of concentration of initiator in reaction.

Table 1. PECH molecular weight, glass transition temperature (Tg) and hydroxyl value

Relationship monomer/initiator	Initiator	Molecular weights(Mn)(g.mol ⁻¹)	Mw/Mn	Tg (°C)	Hydroxyl value(mmol/g)
20:1	SnCl ₄	2974	1.09	-37	0.73 (0.90)
	SnCl ₄ .5H ₂ O	1625	1.11	-37	1.12 (1.24)
60:1	SnCl ₄	1417	1.20	-41	1.16 (1.24)
	SnCl ₄ .5H ₂ O	1033	1.18	-42	1.19 (1.29)

The effect of initiator content on polymer glass transition temperature is clearly observed by DSC curves, which are showed in Fig. 3. Higher initiator content causes an increase of polymer Tg due to higher molecular weight. This effect can be observed as the critical molecular weight was not attained in these polymers. The polymer obtained with the hydrate and anhydrous initiators showed almost the same glass transition temperature, suggesting that water has no influence in glass transition. These results are summarized in Table 1.

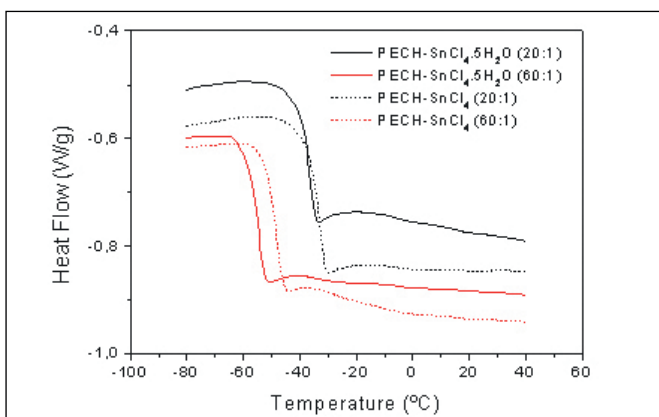


Figure 3. DSC curves for PECH obtained with different catalyst contents.

In Table 1, we can observe that hydroxyl values seem to be directly related to molecular weights, independent of the type of initiator used, hydrate or anhydrous. The rule is: lower molecular weights, higher hydroxyl values. To exclude any doubts, PECH was synthesized again in the same conditions,

Table 2. Percentage of carbon and hydrogen in samples of PECH.

Relationship monomer/initiator	Initiator	Carbon (%)	Hydrogen (%)
20:1	SnCl ₄	38.3	5.7
	SnCl ₄ .5H ₂ O	38.7	5.9
60:1	SnCl ₄	38.6	5.4
	SnCl ₄ .5H ₂ O	38.4	5.8

and results to hydroxyl value to this new synthesis process are exhibited between parentheses, with the same tendency.

Results from elemental analysis of carbon and hydrogen showed close values, where, practically, there is no difference to the same elements. Table 2 exhibits these results.

CONCLUSIONS

Water exert influence in PECH synthesis, carrying out to a lower molecular weight and higher hydroxyl content, but, without altering its backbone structure. Both PECHs, made with hydrate and anhydrous initiator, present the same carbon and hydrogen contents. However, the monomer/initiator relationship deeply alters properties as molecular weights and Tg.

In a general way, PECH, made with hydrate initiators, presents lower molecular weight and higher hydroxyl value of the ideal range to use in synthesis of GAP.

REFERENCES

- Biedron, T. *et al.*, 1991, "Polyepichlorohydrin Diols Free of Cyclics: Synthesis and Characterization", *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 29, No. 5, pp. 619-628.
- Dee, L.A. *et al.*, 1980, "N-Methylimidazole as a Catalyst for Acetylation of Hydroxyl Terminated Polymers", *Analytical Chemistry*, Vol. 52, No. 4, pp. 572-573.

- Eroglu, M. S., Guven, O., 1996, "Spectroscopy and Thermal Characterization of Poly(glycidyl azide) Converted from Polyepichlorohydrin", *Journal of Applied Polymer Science*, Vol. 60, No. 9, pp. 1361-1367.
- Francis, A. U. *et al.*, 2003, "Structural Characterization of Hydroxyl Terminated Polyepichlorohydrin Obtained Using Boron Trifluoride Etherate and Stannic Chloride as Initiators", *European Polymer Journal*, Vol. 39, No. 4, pp. 831-841.
- Frankel, M. B. *et al.*, 1992, "Historical Development of Glycidyl Azide Polymer", *Journal of Propulsion and Power*, Vol. 8, No. 3, pp. 560-563.
- Guanaes, D., *et al.* 2007, "Influence of Polymerization Conditions on the Molecular Weight and Polydispersity of Polyepichlorohydrin", *European Polymer Journal*, Vol. 43, No. 5, pp. 2141-2148.
- Mohan, Y.M. *et al.*, 2004, "Synthesis, Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Units", *Journal of Applied Polymer Science*, Vol. 93, No. 5, pp. 2157-2163.
- Okamoto, Y., 1984, "Cationic Ring-Opening Polymerization of Epichlorohydrin in the Presence of Ethylene Glycol", *Polymer Preprints*, Vol. 25, No. 1, pp. 264-265.
- Qureshi, M. Y., Ochel, M., 1996, "Synthesis and Characterization of High Molecular Weight Poly (Trimethylene Oxide)", *European Polymer Journal*, Vol. 32, No. 6, pp. 691-693.
- Sciamareli, J. *et al.*, 2009a, "Síntese e Caracterização do Polímero Energético Metil Azoteto de Glicidila (GAP) Via Análises Instrumentais", *Polímeros: Ciência e Tecnologia*, Vol. 19, No. 2, pp.117-120.
- Sciamareli, J., *et al.* 2009b, "Otimização do Processo de Obtenção do Pré-Polímero Metil Azoteto de Glicidila", *Journal of Aerospace Technology and Management*, Vol.1, No. 1, pp. 29-34.
- Silverstein, R.M. *et al.*, 1981, "Spectrometric Identification of Organic Compounds", John Wiley & Sons Inc., New York, USA.