

Synthesis and Thermal Characterization of Silicon-based Hybrid Polymer

Silvia A. C. Abarca^{*a}, Octávio Flores^b, André. L. G. Prette^b, Gilvan. S. Barroso^b,
 Thais Coan^a, Günter Motz^b, Ricardo A. F. Machado^a

^aFederal University of Santa Catarina, Department of Chemical Engineering - Brazil

^bUniversität Bayreuth, Lehrstuhl Keramische Werkstoffe - Germany
 silvia@enq.ufsc.br

Synthesis of hybrid organic-inorganic silicon based polymers has attracted a great interest due to the potential combination of the well-known mechanical properties of organic polymers with the attractive thermal stability of inorganic polymers. Organic polymers are formed by long carbon-carbon bonding chains with functional groups attached to them while inorganic silicon-based polymers are usually constituted of silicon in combination with elements such as nitrogen, oxygen or carbon. The aim of this work was to obtain a hybrid polymer with unique characteristics such as excellent thermal stability, low heat release rate, high heat resistance, slow burning rate without a flaming drip and limited release of toxic gases during thermal decomposition by incorporating quantities of polysilazane on polystyrene matrix by radical polymerization reaction. Bulk polymerization and solvent polymerization were chosen as methodology to obtain the product. For the polymerization, the polysilazane HTT1800 (inorganic precursor) and the organic monomer styrene were used, while dicumyl peroxide was chosen as a radical initiator. The polymerization reaction was carried out at high temperature and under argon atmosphere. A glass reactor with a condenser was used to avoid solvent loss and temperature was controlled by thermostatic bath. Subsequently, when (1-methylethyl) was used as a solvent, it was removed by vacuum distillation. Chemical and physical properties of the hybrid organic-inorganic polymer were analysed through Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Fourier Transformed Infrared (FTIR) and Flammability Analysis (in accordance with UL94).

1. Introduction

Polymeric materials have been extremely necessary to electronics, aerospace, textiles, household products, automobiles, and the packaging industry, making possible creation of many products and also as a substitute for high cost raw material. Polymers present a good combination of chemical and physical properties, can be easily processed and are recyclable. Polystyrene which is one of the most used polymers nowadays, the flammability presented when this polymer is exposed to a heat source is extremely high.

The improvement of fire resistance for flammable polymeric material represents an alternative to allow some applications which were earlier not possible. Different alternatives have been used as halogen based compounds (Cortemiglia et al., 1987), metal hydroxides (Bains e Cusack, 1990), nanocomposites (Zaitsev et al., 2007), nitrogen based compounds (Gaan et al., 2008), phosphorus based compounds (Beach et al, 2008) and silicon based compounds (Chen e Jiao, 2009). At the present time halogen based compounds have been an excellent alternative, with a high efficiency observed as flame retardant (FR). Nevertheless the combustion of halogen-based compounds generates the formation of smoke with a number of negative characteristics (Camino et al., 1991). Nowadays, plastic industry is suffering hard pressures from health organizations which are against the use of halogen-based FR. Searching for an

environmental safety FR option studies about different kind of halogen free flame retardant has started (Fu et al., 2000 and 2001).

A great number of studies on silicon-based compounds, principally with siloxane (Tang et al., 2011), have been done. Some good improvements can be achieved when inorganic compounds are used as additive or adding it to the backbone chain e.g. these additives can form physical networks during polymer melt that may reduce dripping, act by dilution effect or even reduced heat feedback (Marosi et al., 2002). Meanwhile another group of silicon based compound, silazane molecules, also present interesting properties to flame retardancy field.

It is known that poly(vinyl)silazane, a preceramic polymer, have many physical and chemical properties, such as excellent thermal stability, good mechanical properties, good thermal conductivity and oxidation resistance (Nighiem et al., 2007).

This work intends to reduce the flammability of polystyrene by proposing the synthesis of a hybrid polymer, using radical polymerization of organic and inorganic monomers.

2. Experimental

HTT 1800 obtained from Clariant was used as a flame retardant compound and inorganic monomer. While Styrene obtained from Sigma Aldrich was used as organic monomer.

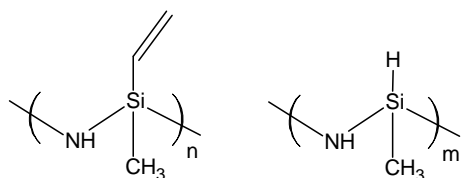


Figure 1 – HTT 1800

The reaction was performed using a batch stirred glass reactor coupled with a condenser and an oil bath with controlled temperature. The ratio of organic monomer to inorganic monomer used in the reaction was 3:1. Both solvent and bulk polymerization was used to obtain the hybrid polymer and dicumyl peroxide, obtained from Sigma Aldrich, was used as radical initiator. When necessary, (1-methylethyl) benzene was applied as solvent phase. Firstly the organic monomer was added into a glass reactor at room temperature. An oil bath was used to heat the glass reactor. The glass reactor was then heated until 90 °C when the inorganic compound was added under higher RPM. The mixture was heated until 100 °C and dicumyl peroxide was then added. All compounds were mixed and the temperature was increased until 135 °C. After polymerization, the solvent (1-methylethyl) benzene was removed with rotary evaporator and vacuum. All procedures were executed under Argon atmosphere.

2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a thermogravimetric equipment, Linseis L81 A1550 model thermogravimetric equipment. Samples (10-15 mg) for TGA analysis were heated at 10 °C/min to 1000 °C under Argon atmosphere. TGA analysis was important to observe the mechanism of action adopted by flame retardants.

2.2 Differential scanning calorimetry analysis (DSC)

Differential scanning calorimetry analysis (DSC) was carried out with a differential scanning calorimetry equipment from TA Instruments model Q1000. Samples (5-20 mg) for DSC analysis were heated at 10 °C/min to 300 °C under Argon atmosphere. DSC analysis was used to monitor heat effects associated with transitions and chemical reaction as a function of temperature.

2.3 Fourier Transformed Infrared (FTIR)

Fourier Transformed Infrared (FTIR) was performed with FTIR equipment from Bruker Optics model Bruker Tensor 127. The FTIR was coupled with TGA to measure which substances were generated during TGA analyses.

2.4 Flammability analysis

Flammability test was performed with the aid of Frenzeli Werke GmbH in accordance with UL94 – Test for Flammability of Plastic Materials for Parts in Devices and Appliances (horizontal samples). The analysis involves samples of hybrid polymer that was prepared as plaques with 150 mm x 50 mm X 13 mm. The

apparatus is manually operated moving a burner ignition source under of the plaque sample to apply a flame from the source to the sample according to the UL 94 regulations.

3. Results

3.1 Thermogravimetric analysis (TGA)

Figure 2 show thermogravimetric results for pure monomers and hybrid compositions made by bulk and solvent polymerization.

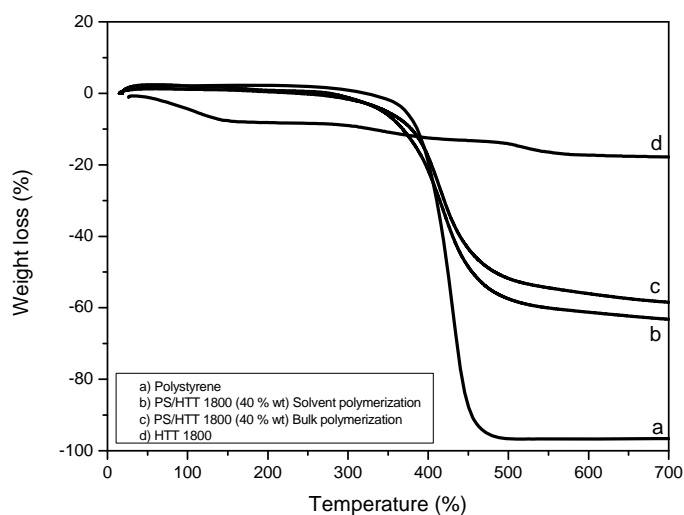
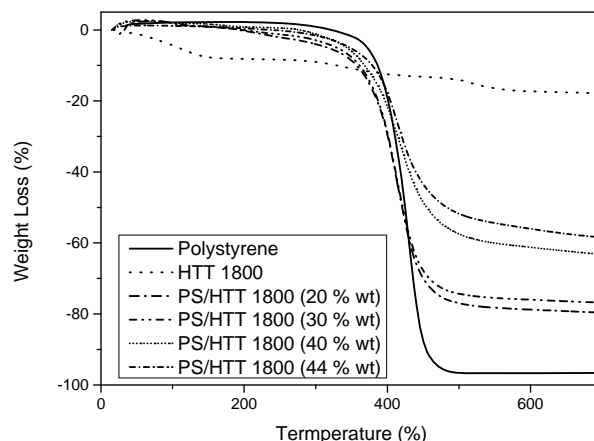


Figure 2 – Thermogravimetric analysis of pure HTT 1800, pure polystyrene, PS/HTT 1800 bulk and PS/HTT 1800 solvent polymerization.

It was possible to observe a decrease of weight loss when pure polystyrene is compared to hybrid compounds obtained from the reaction between polystyrene and HTT 1800. For products from PS/HTT 1800 bulk polymerization (Figure 2, line c) was obtained around 57 % of weight loss and around 60 % of weight loss for solvent polymerization products (Figure 2, line b). Pure polystyrene (Figure 2, line a) presented 100% weight loss. Another important point is the temperature when polymer or hybrid polymer starts to decompose, or degradation temperature. For pure polystyrene and PS/HTT 1800 obtained by bulk polymerization, the initial decomposition temperature was around 400 °C. Although for PS/HTT 1800 obtained by solvent polymerization was observed an initial decomposition at 200 °C as a first step. This behaviour is typically observed in condensed phase flame retardant systems where a protective layer is

initially formed. Another study with different concentrations of inorganic monomer was performed. Results



are shown in Figure 3.

Figure 3 – Thermogravimetric analysis of pure HTT 1800, pure polystyrene, PS/HTT 1800 in different concentrations of HTT 1800 reacted by solvent polymerization.

With increase in concentration of HTT 1800, a decrease of weight loss was observed. No difference between curves related to degradation mechanism was observed.

3.2 Differential scanning calorimetry analysis (DSC)

Figure 4 show the differential scanning calorimetry results for pure monomer and hybrid compositions made by bulk and solvent polymerization.

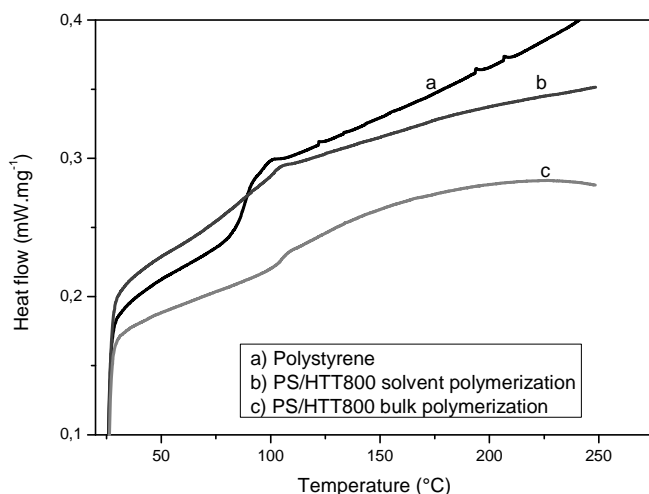


Figure 4 – Differential Scanning Calorimetry of pure polystyrene, PS/HTT 1800 bulk and PS/ HTT 1800 solvent polymerization.

From the DCS analysis was possible to observe the degree of dispersion between both organic and inorganic compounds related to glass transitions values. In Table 1 are values of glass transition temperatures (T_g) for pure polystyrene and organic-inorganic compounds.

Table 1 – Glass transition temperatures values for pure polystyrene, PS/HTT 1800 bulk and PS/HTT 1800 solvent polymerization

Sample	T _g (°C)
Polystyrene	83.51
PS/HTT 1800 (solvent polymerization)	90.99
PS/HTT 1800 (bulk polymerization)	101.74

A significant increase of glass transition was observed when pure polystyrene is compared to both PS/HTT 1800 bulk and solvent polymerization. The highest increase was observed for PS/HTT 1800 bulk polymerization. This behaviour could be due to the reaction between organic and inorganic monomers. During radical polymerization, double vinyl bond of styrene suffer a rupture caused by radical initiator. Radical initiator produce active monomers that can react between themselves or can also react with double bonds from HTT 1800. With these reactions between double bonds of both, polystyrene and HTT 1800, is possible to obtain polystyrene with some quantity of inorganic monomer connected into polymeric matrix. Some additional analyses are necessary to confirm if this inorganic molecule is bonded as a pendant group which can react with other styrene monomers or with other HTT 1800 molecules to execute a crosslinking reaction.

3.3 Thermogravimetric analysis monitored by Fourier Transformed Infrared (TGA-FTIR)

The pyrolysis products formed during TGA analysis were monitored using TGA-FTIR. FTIR spectra of pyrolyzed products are shown in Figure 5.

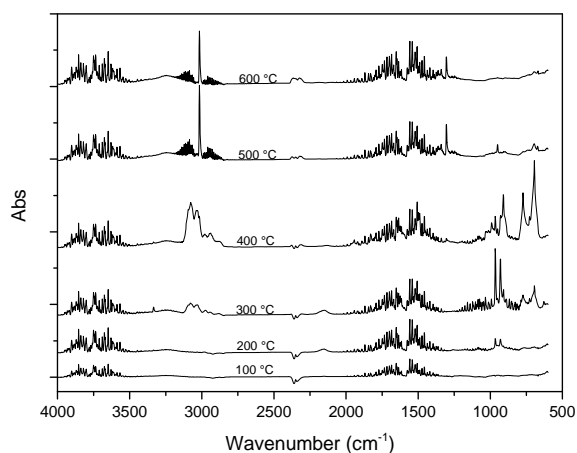


Figure 5 – FTIR-TGA PS/HTT1800 bulk and PS/HTT 1800 solvent polymerization.

At 200 °C (PS/HTT 1800) the absorbance peak of N-H groups was observed at 1000 cm⁻¹. The presence of absorbance peak at 1500cm are assigned to the formation of N-H groups at 200 °C and 300 °. The N-H groups are important volatiles for flame retardant systems for two reasons: at high temperatures ammonia is liberated and can act as diluents for oxygen and combustible gas mixtures and can also promote recombination with reactive radicals to form more thermally stable molecules. Some residues can be formed in the condensed phase resulting in endothermic process, this is another way of protection of flame retardants. Some N-H groups are useful to help in intumescent process and formation of protective layers. At 400 °C, the C-H groups were liberated at absorbance peak of 3000 cm⁻¹. C-H liberated during pyrolysis is responsible in the formation of a protective layer with high thermal resistance. This protective layer is generally formed between the gaseous phase (where combustion takes place) and the solid phase. The layer is important to limit the transfer of volatile gases and oxygen and also acts as a physical barrier for solid products (Laoutid et al., 2008). At 500 °C, the Si-H group was released which is another important group at absorbance peak 2200 cm⁻¹. It is known that small quantities of silicon-based compound can

improve flame resistance due to the ability of performing cross linked reactions with vinyl groups of styrene and also due to its thermal resistance.

3.4 Flammability analysis (UL94)

Flammability tests were executed with pure polystyrene and samples from PS/HTT 1800 bulk polymerization and PS/HTT 1800 solvent polymerization. Polystyrene sample was totally burned with drops of polymer during the test. Samples of PS/HTT 1800 presented some flame retardancy with a time to flame extinction below than 30 s and no dripping was observed. According to the results obtained, the hybrid material was classified as a V-1. To achieve a higher degree of flame retardancy, another flame retardant can be applied to improve some deficiency of protection mechanism.

4. Conclusions

In this study a hybrid organic inorganic compound was synthesized by adding some quantities of HTT 1800, an inorganic monomer with the aim of improving flame retardancy of polystyrene. TGA analyses show a decrease of weight loss of polystyrene when polysilazane was added. Both bulk and polymerization appears to be a good synthesis method to reduce the weight loss of polystyrene.

DSC analyses also shown a higher increase of glass transition temperature for PS/HTT 1800 obtained by bulk polymerization. This behavior is probably due to cross linking reactions between organic and inorganic monomers creating material with enhanced thermal resistance. Results from TGA-FTIR show that a quantity of important groups was liberated with the increase of temperature. In a flame retardant system those groups probably act in gas phase, reacting with combustible species and obtaining more stable compounds. Flammability analysis demonstrated that flame extinction was not the main mechanism of protection, once a big quantity of polysilazane was applied and extinction time was not efficient as expected. Although, no dripping was observed during tests. This behavior is typically observed in flame retardants which act preferentially by condensed phase mechanism.

Acknowledgements

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