Thermal behavior of poly(2-hydroxyethyl methacrylate-bis-[trimethoxysilylpropyl]amine) networks

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Abstract. Poly(HEMA-BisSi) networks were prepared by using acid-catalyzed sol-gel of bis-[trimethoxysilylpropyl]amine (BisSi) and free radical polymerization of 2-hydroxyethyl methacrylate (HEMA). The thermal properties of the poly(HEMA-BisSi) networks were investigated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermal behavior of these networks was also compared with homopolymers (The networks formed in both PHEMA and PBisSi gels were identified). The glass transition temperature (Tg) of PHEMA homopolymer was found as 103.74 °C. The thermal degradation of the poly(HEMA-BisSi) networks with different silica contents (e.g. 10, 15 and 25 wt%) were evaluated with use of DTG. It was observed that the thermal degradation temperature of poly(HEMA-BisSi) networks changed much with the BisSi content.

1 Introduction

Poly(2-hydroxyethyl methacrylate)(PHEMA) have been widely used in the pharmaceutical industry because of biocompatibility and friendly characteristics[1-7]. It is interesting to study how the thermal stability of PHEMA of is affected by incorporating BisSi (bis-[trimethoxysilylpropyl] amine). It is interesting choice because its hydroxyl groups, in addition to forming hydrogen bonds will eventually form Si-O-C by condensation with silanol groups[8,9,15]. Consequently, design of efficient response active materials that are also thermally stable has been a long sought after goal [10].

The use of sol-gel method [11-13] form synthesis of new materials is particularly appealing because the low temperature solution-based synthesis route is amenable to molecular chemistry approaches such that one can modify the structure and function of the parent silica glass by structure modification of the precursor. One strategies involves the simultaneous growth of the inorganic phase via acid hydrolysis and condensation of alkoxysilane precursor and the polymer phase via free radical polymerization of vinyl monomer in a common solvent [8].
In this study, we report the thermal properties of poly(2-hydroxyethyl methacrylate-bis[trimethoxysilylpropyl]amine) networks.

2 Experimental

Into in three-neck flask were placed BisSi, HEMA, THF and HCl, equipped with a condenser, a magnetic stirrer and a nitrogen gas inlet-outlet. Polymerizations were carried out in an inert gas atmosphere. In a typical procedure for the preparation of 15 wt% SiO$_2$ poly(HEMA-BisSi) hybrid material, 51.22 g (0.15 mol) of bis-[trimethoxysilyl-propyl]amine and 45.07g (0.346 mol) of HEMA were dissolved in 36.05g(0.50 mol) of THF at room temperature. Then, 1.250 g of 0.5 M HCl was added to solution. The solution was refluxed at 70 °C for 2.5 h. After the polymer solutions was cooled to room temperature, 0.0042 g (0.017 $10^{-3}$ mol) of benzoyl peroxide (BPO) was added to the solution and dissolved. At room temperature, the solvent (i.e. THF) and by-products from sol-gel reactions (i.e. MeOH and water) were removed via vacuum distillation. The transparent solutions were finally dried for 12 h in an oven at 80°C to complete the polymerization. The resulting xerogels (powders) formed were comminuted in an agate mortar for subsequent analysis [8].

2.2 Materials

Bis-[trimethoxysilylpropyl]amine (BisSi, Aldrich) and 2-hydroxyethyl methacrylate (HEMA, Aldrich), tetrahydrofuran anhydrous (THF, Aldrich), benzoyl peroxide (BPO, Aldrich) and hydrochloric acid (HCl, J.T. Baker) were used without further purification.

2.3 Measurements

Thermalgravimetric analyses (TGA) were conducted (Netzsch, instrument STA449F3 Jupiter) by heating powdered samples to 800 °C at 10 °C with a flow of 20 mL N$_2$/min. The random errors of weight losses were determined for samples with selected compositions. Differential scanning calorimetry (DSC) traces were recorded (Netzsch, instrument STA449F3 Jupiter).

3 Results and discussion

The use of bis-[trimethoxysilylpropyl]amine (BisSi) as the sole component in a coating is limited, however, as gelation occurs soon after mixing with water [14]. The bis-alcoxysilan (BisSi) and HEMA (via free radical polymerization) after addition of HCl are likely to under hydrolysis and condensation reactions that occur either by elimination of methanol or water molecules. The hydrolysis of BisSi and HEMA (Scheme 1) may involve the following reaction steps:

![Scheme 1](attachment:image)
3.1 Thermal analyses

3.1.1 DSC

DSC sensitively detects the small heat capacity change due to the glass transition temperature for PHEMA and the poly(HEMA-BisSi) networks (Figure 1). DSC measurements performed on the hybrid polymers revealed that did not have a significant glass transition temperature \( T_g \) and the \( T_g \) of the baseline polymer, PHEMA, at about 103.74\(^\circ\)C. This lack of observable transition in the poly(HEMA-BisSi) samples is most likely attributable to the influence of the crosslinking that occurs via crosspolymerization of the growing PBisSi polymer chains with HEMA pendant groups on the silica structure formed by the condensation of PHEMA with the silica. Costa R. [15] and Li S. [8] reported effect over the behavior the hybrids materials in DSC similar to this results.

![Figure 1](image)

**Figure 1** DSC thermograms of Poly(HEMA-BisSi) networks containing different content of BisSi (10, 15, 25 wt%) and homopolymers. (a)PHEMA, (b)PBisSi, (c) Poly(HEMA-BisSi)10%1.5, (d) Poly(HEMA-BisSi)15%1.5 and (e) Poly(HEMA-BisSi)25%1.5.

3.1.2 TGA

To examine the composition effect on thermal degradation poly(HEMA-BisSi) networks, we measured TG-curves for all the samples from 27 to 800 °C. The poly(HEMA-BisSi) hybrid polymer show improved thermal stability as observed by a reduction in mass loss rate from the TGA measurements in \( \text{N}_2 \) atmosphere (Figure 2). The results of TGA analyses show that the weight loss for all hybrids occurs in two steps. The first step is due to the evaporation of non-bonded water and other volatile compounds from room temperatures to ~200 °C [15]. The second step, is due polymer degradation and loss of formation a percolated poly(HEMA-BisSi) network [8]. From DTG curves, the maximum temperature of weight loss were also noted in Figure 3 the mass loss of PBisSi begins at 496.92 °C and at maximum temperature 517.23 °C, such as shown in the Figure 3. However, initial degradation temperatures of poly(HEMA-BisSi) networks were increased slightly in all samples compared with PHEMA and with increasing BisSi content. As can be seen Figure 2 poly(HEMA-BisSi) networks degrade in two steps. This is evidenced by appearance of distinct peaks in DTG thermograms. On the other hand, the mass loss of PHEMA reaches maximum at 428.71 °C. The curve
of PHEMA homopolymer indicates one reaction stage (Figure 3) which is reflected as single peak in the DTG curve (Figure 3).

![Graph of TGA curves for PHEMA, PBisSi, Poly(HEMA-BisSi)10%1.5, Poly(HEMA-BisSi)15%1.5, and Poly(HEMA-BisSi)25%1.5.](image1)

4 Conclusions

The results clearly demonstrate that this approach would allow for the synthesis of organic-inorganic materials by conventional casting. Based on the TGA results and DTG observation of the stability of poly(HEMA-BisSi) networks, a stabilization model is proposed. The weakly acidic silanol group (−OH) on the silanol products and groups (−OH) on the PHEMA, forms hydrogen bonds with the strongly secondary amine group (−NH) on the PBisSi. On the other hand, \( T_g \) of the poly(HEMA-BisSi) networks cannot be determined with accuracy.

Acknowledgements

To BUAP-CUV and DGEST-4416.11-P for the financial support.

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