



Thermal behaviour and flame retardancy of polyurethane high-solid coatings modified with hexakis(2,3-epoxypropyl)cyclotriphosphazene

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ABSTRACT

Hexakis(2,3-epoxypropyl)cyclotriphosphazene was employed for preparation of high – solid hybrid organic-inorganic poly(urethane-cyclophosphazene) coatings based on epoxy-terminated urethane oligomer which were cured with ethylenediamine. The flame retardancy, thermal degradation behavior and some surface properties of the coatings were investigated. The results of thermogravimetric analysis suggested that thermal degradation of poly(urethane-cyclophosphazene) occurred in two main stages and the introduction of cyclophosphazene resulted in increase of thermal stability. The main gases released during thermal decomposition of the samples were carbon dioxide, ammonia, water and tetrahydrofuran. The microscale combustion calorimetry revealed that the maximum specific heat release rate and the heat release capacity of the hybrid materials decreased significantly with incorporation of cyclotriphosphazene. The water contact angle and gloss decreased while hardness increased with the increase of hexakis(2,3-epoxypropyl)cyclotriphosphazene contribution in the coating.

1. Introduction

Polyurethanes (PUs) are a class of segmented polymers build of alternating hard segments deriving from diisocyanate and chain extender and soft segments comprising polyol. Due to their structure, PUs offer very good elasticity, high mechanical strength, hardness, and abrasion resistance. These polymers are employed in wide variety of applications, such as foams, elastomers, adhesives, and coatings [1,2].

However, polyurethanes as other organic polymers are also known for their relatively high flammability; accompanied by the production of corrosive or toxic gases during combustion. To improve these properties modification by incorporation of various fire retardants (FR) was employed [3]. The FR can be chemically bonded with polymer or physically mixed with polymer matrix. The principal advantage of application of reactive flame retardants, compared to other flame retardant additives, is that they can be used in relatively low concentrations. Additionally, those kind of FR can limit the damage caused by heterogeneous additives to the mechanical properties of the materials and reduce the migration of the flame retardant onto the material surface [4].

Due to some disadvantages related to the generation of toxic and

corrosive gases during thermal degradation of commonly used FR, containing halogen atoms other non-halogen flame retardants including cyclotriphosphazenes were developed [5]. Cyclotriphosphazenes are compounds containing an inorganic ring composed of three P = N units that can be synthesized from hexachlorocyclotriphosphazene. Depending on the type and properties of the substituents, they can show very different physical and chemical characteristics in various systems [6–8].

The thermal properties and flame retardancy of cyclotriphosphazenes modified polymers results from phosphorous and nitrogen flame-retardant synergy. The thermal decomposition of the phosphazene-based polymers is an endothermic process, and phosphate, metaphosphate, polyphosphate generated in the thermal decomposition form a nonvolatile protective film on the surface of the polymer isolating it from the air. Additionally, the non-flammable gases released such as CO₂, NH₃ and N₂ cut off the supply of oxygen so as to achieve the aims of synergistic flame retardancy [9]. The phosphorus-based FR are among the most effective combustion inhibitors and can volatilize into the gas phase, to form active radicals (PO₂·, P·O and HP·O), and act as scavengers of H· and OH· radicals. However, it was noted that the phosphorus-based flame retardants are significantly more effective in

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oxygen- or nitrogen-containing polymers, thus, they can be employed for PU modification [4,10].

So far, for modification of polyurethanes were employed cyclotriphosphazenes with various reactive derivatives substituents i.e. hydroxyl [10–14], methacryloxy [15] or aziridinyl [16]. Application of multifunctional cyclotriphosphazene for the preparation of crosslinked PU resulted in increase of the tensile strength and thermal stability and reduction of elongation [17]. There are also studies concerning modification of polyurethanes by linear polyphosphazenes [18] or fluorine-containing polyphosphazenes [19] showing increased hydrophobicity.

However, little is known about the influence of epoxyfunctional cyclotrisiloxane on thermal behavior and flame retardancy of polyurethane high-solid systems. From our earlier studies it results that those kind of low viscosity systems based on epoxy-functional urethane oligomer which is cured by means of an amine can be employed as environmental friendly coatings [20]. Hence, the aim of this work is to investigate the effect of hexakis(2,3-epoxypropyl)cyclotriphosphazene on surface properties, thermal behavior, and flame retardancy of polyurethane high-solid coatings composed of epoxy-terminated urethane oligomer cured with diethylenetriamine.

2. Experimental

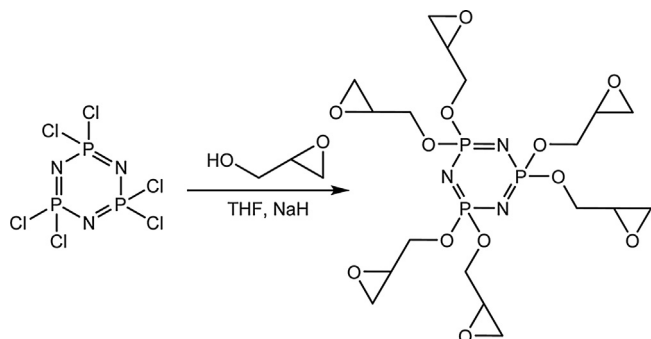
2.1. Materials

Toluene diisocyanate (TDI), glycidol, diethylenetriamine (DETA) and dibutyltin dilaurate (DBTDL) from Aldrich were used without further purification. Poly(oxytetramethylene)diol (PTMO, Mn = 1000), was purchased from Aldrich and dried in a vacuum oven at 105 °C before use. Sodium hydride (NaH), tetrahydrofuran THF, hexachlorocyclotriphosphazene (ClCP) and 2,3-epoxypropane-1-ol for synthesis of hexakis(2,3-epoxypropyl)cyclotriphosphazene (ECP) were used as supplied (Aldrich) without any additional pretreatment.

2.2. Synthesis of hexakis(2,3-epoxypropyl)cyclotriphosphazene (ECP)

NaH (8.28 g, 0.345 mol) and 100 ml of dry THF was placed in three neck, round bottom flask equipped with thermometer, condenser and magnetic stirring bar and was cooled down to 0 °C. Next 2,3-epoxypropane-1-ol (25.57 g, 0.345 mol) diluted in 50 ml of THF was added drop by drop to the mixture. After 1 h of mixing at 0 °C hexachlorocyclotriphosphazene (20 g, 57.53 mmol) in 100 ml THF was added dropwise to the flask. The reaction was maintained for 24 h at room temperature and 2 h in THF boiling temperature. Reaction progress was controlled with FT-IR spectroscopy. After the reaction the mixture was cooled and the resulting precipitate was filtered off and washed with THF and dried. 27.39 g of colorless oil was obtained (yield 83%). The synthesis was presented on Scheme 1. The formation of the desired product was verified by NMR and FTIR analysis:

^1H (CDCl₃; δ (ppm)): 2.61 (6H, CH₂-CH(O)-CH₂(O)); 2.76 (6H,



Scheme 1. Synthesis of hexakis(2,3-epoxypropyl)cyclotriphosphazene (ECP).

CH₂-CH(O)-CH₂(O)); 3.19 (6H, PO-CH₂-CH(O)); 3.85 (6H, PO-CH₂-CH); 4.12 (6H, PO-CH₂-CH).

^{13}C (CDCl₃; δ (ppm)): 44.51 (CH₂-CH(O)-CH₂(O)); 50.03 (PO-CH₂-CH(O)); 66.84 (PO-CH₂-CH)

^{31}P (CDCl₃; δ (ppm)): 17.90

FT-IR (cm⁻¹): 3003 (C-H); 2947 (-CH₂); 1213 (P = N ring); 1012 (P-O-R); 906 (epoxy).

2.3. Synthesis of epoxy-terminated urethane oligomer (EPU)

The epoxy-terminated urethane oligomer (EPU) was obtained in a two-step synthesis. At the 1st stage TDI was placed in 100 ml three-necked flask equipped with a heating mantle, mechanical stirrer, thermometer, reflux condenser and nitrogen inlet. Then PTMO and DBTDL (0.02 wt.% with reference to PTMO) as catalyst were to the flask. The reaction was allowed to proceed at 65 °C till the content of unreacted isocyanate groups reached half of initial value (ca. 30 min). Then temperature was lowered to 30 °C and at the 2nd step glycidol was dropwise added. The temperature was increased slowly during the synthesis to about 70 °C to complete the termination reaction. The reaction was continued until NCO peak at 2270 cm⁻¹ disappeared totally at the FTIR spectra of samples taken from the reaction flask every 1 h. The molar ratio of TDI: PTMO: Glycidol was 2:1:2. The obtained product was characterized by ^1H , ^{13}C NMR and FT-IR spectroscopy.

2.4. General procedure of synthesis of polyurethanes modified with hexakis(2,3-epoxypropyl) cyclotriphosphazene (PUP)

Required amount of epoxy-terminated urethane oligomer (EPU) and/or hexakis(2,3-epoxypropyl) cyclotriphosphazene (ECP) as well as the appropriate amount of diethylenetriamine (1:1 molar ratio of epoxy:NH groups) were placed in a beaker according to formulation presented in Table 1. The beaker content was stirred over hot plate. Then the composition was poured slowly into a clean polytetrafluoroethylene or glass plates and cured first at 100 °C for 5 h and then at 150 °C for 6 h. Using the above procedure 4 samples of cross-linked poly(urethane-cyclophosphazene) materials with varying amount of cyclophosphazene (1, 5, 10, 20 wt.%) were obtained. Additionally, a reference sample of crosslinked EPU was prepared.

2.5. Measurements

2.5.1. NMR spectroscopy

^1H and ^{13}C NMR spectra were recorded with the use of the spectrometer FT NMR Bruker Avance 500^{II}. The samples were dissolved in CDCl₃ and the solution with the concentration of about 0.2 g dm⁻³ was prepared. TMS was used as a standard.

2.5.2. IR spectroscopy

FT-IR spectra were recorded on a Nicolet iS10 (Thermo Scientific) Fourier transform spectrophotometer equipped with a diamond ATR unit. In all cases 16 scans at a resolution of 4 cm⁻¹ were collected, to record the spectra in a range of 4000–650 cm⁻¹.

Table 1
Chemical composition of poly(urethane-cyclophosphazene) materials.

Sample	Wt.% of ECP with reference to ECP + EPU	Wt.% of ECP in the sample	Wt.% of EPU in the sample	Wt.% of DETA in the sample
PUP0%	0	97.3	0.0	2.7
PUP1%	1	96.2	0.9	2.9
PUP5%	5	91.7	4.8	3.5
PUP10%	10	86.0	9.6	4.4
PUP20%	20	74.9	18.8	6.3

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