Polymer Degradation and Stability 101 (2014) 40–51

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Thermal degradation and fire behaviour of novel polyurethanes based on phosphate polyols

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ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form
26 December 2013
Accepted 12 January 2014
Available online 22 January 2014

Keywords:
Polyether polyol
Flame retardant
Phosphate
Coating

ABSTRACT

The development of new polyurethane coatings with enhanced flame retardant properties based on the phosphorylated polyols is explored. The incorporation of phosphorus into the polymer molecular structure took place by reacting polymeric MDI with polyether polyols based on an alkoxylated glycerol phosphate initiator. The structure of the coatings was confirmed by FT-IR spectra. The thermal stability and flame retardant properties of the coatings were characterized using TGA, TGA-MS. LOI test, cone calorimetry, SEM microscopy and EDAX analysis. The results have highlighted the importance of the phosphorus chemical environment and its influence on the thermal degradation and oxidation of the polyol under different atmospheres.

1. Introduction

Polyurethane (PU) coatings have a large number of applications such as protecting from moisture, ionic contaminants, particulates and fire, and various substrates such as wood, plastics, metal, glass, textile and ceramics [1]. Fire retardant coatings have been widely used as one of the easiest, oldest and most efficient ways to protect material against fire. Ideally, they should have several advantages such as the maintaining of the mechanical properties, easy processing, and the possibility of the application of multiple substrates, such as metallic materials, plastics, textiles, and wood [2,3]. In addition, PU coatings are often used as passive fireproofing material, which decreases heat transfer from a fire to the object that is protected [4].

Recent patents and technical reports indicate a growing interest in halogen-free systems most of them focused on phosphorus-based flame retardants. The most common method for incorporating phosphorus is blending an inorganic- or organic-based phosphorus compound into a polymer during processing [5–7], as additive or reactive into the PU formulation. PU materials containing phosphorus not chemically bonded to the polymer chain have the disadvantages of being susceptible to being released with time [8], poor compatibility and creating heterogeneities in the material that can produce a worsening of the mechanical properties of polymers [8–10]. However, the incorporation of phosphorus into the molecule has the advantages of permanent attachment and perfect homogeneous distribution, and requires smaller amounts of flame retardant agent [9]. Consequently, this way of phosphorus incorporation in the material should have a much smaller influence upon the physical and mechanical properties of the polymer [8]. On the other hand, phosphorus compounds perfectly linked and incorporated in the polymer demonstrate a notable effectivity of the phosphorus-carbonaceous char formation [1,9]. They have also several advantages such as low toxicity and corrosivity, as well as producing low smoke during burning [2–5].

Generally, compounds containing phosphorus such as phosphate, phosphonates, phosphites, phosphine oxides and phosphonium compounds are considered to be one of the most efficient environmental friendly flame retardants. Several methods have been used to prepare various phosphorated coatings. The work of El Khatib et al. (2003) was focused on to the synthesis of phosphonate diols as chain extenders for the preparation of polyurethane elastomers [8]. Banks et al. (1993) reported on the phosphorylation of

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0141-3910/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2014.01.012

poly(vinyl alcohol) and poly(ethylene-co-vinyl alcohol) [10]. Park et al. (2001) synthesized pyrophosphoric lactone-modified polyester that contains two phosphorus functional groups in its base resin structure unit [11].

Our research group has already developed the employment of phosphated initiator for the synthesis of polyether polyols by anionic ring-opening polymerization, according to previous studies of Velencoso et al. [12,13]. This route opens up the possibility of preparing a new range of products with enhanced flame retardant properties. In addition, in order to develop a competitive polymerization process, our objective was mainly centred on developing systems where an initiator is used as received and where bulk processes are favoured. Most of this research has been focused on the use of glycerol phosphate disodium salt as an initiator, caesium hydroxide as a catalyst, dimethyl sulfoxide (DMSO) as an aprotic solvent and propylene oxide as a monomer. The main aim of this current work was to investigate the effectiveness of phosphorylated polyols as a reactive-flame retardant for coatings. A commercially feasible and cost-effective material is intended to be developed. The second aim was focused on the research of the burning of the coatings in order to apply these flame retardant materials as fire barriers for a substrate with industrial application.

2. Experimental

2.1. Materials

The raw materials employed in polyurethane coating synthesis were Suprasec 2237 (polymeric methane diphenyl diisocyanate) characterized by NCO% = 22.7, average functionality = 2.5; Daltocel F435 (flexible polyether polyol), M_w = 1920 g/mol, hydroxyl value = 56 mgKOH/g; Daltolac R535 (rigid polyether polyol), M_w = 380 g/mol, hydroxyl value = 585 mgKOH/g; methyl propyl diol (glycol chain extender), M_n = 90 g/mol, hydroxyl value = 1247 mgKOH/g; TEP (triethyl phosphate); BYK A530 (defoamer); Sylosiv A3 (moisture scavenger). All raw materials were supplied by HUNTSMAN-Polyurethanes. All other reagents and solvents used in the study were analytical grade and used as delivered.

The reactive flame retardant used is β-glycerol phosphate disodium salt pentahydrate (GPNa; 98%, Sigma–Aldrich) which is incorporated into the polymeric structure of the phosphorylated flexible polyether polyols.

2.2. Preparation of coatings

The coating formulation is reported in Table 1. The synthesis of phosphorylated flexible polyether polyols was carried out according to previous studies of Velencoso et al. [13]. The phosphorus content in the PU depends on the type of phosphorylated polyol used for each coating. To get the optimal ratio of the monomer to initiator, all polyols were synthesized with 0.96 mol of glycerol phosphate disodium salt as an initiator and catalyst/initiator molar ratio of 1:6 using CsOH as a catalyst, in order to obtain molecular weights between 1500 and 2000 g/mol and phosphorus content between 0.5 and 1.5 wt.%, as shown in Table 2. In the coating formulation, Daltocel F435 was replaced by the phosphorylated polyols, PGP1, PGP2, PGP3, PGP4 and PGP5. The recipe of the PU coatings was calculated taking into consideration the hydroxyl number. This OH_v corresponds with the hydroxyl number of the polyol chain and the hydroxyl number of the phosphate groups linked to the polyol chain, as shown in Scheme 1. As expected, the high OH_v of the phosphorylated polyols leads to an increase of reactivity and end-cure of the coating. Thereby, the addition of a catalyst was not necessary. The phosphorylated polyols were incorporated alone without other reactive flame retardant compound.

Table 1
Weight percentage of raw materials for PU coatings.

Raw material	REF coating (part by weight)	Phosphorylated coating (part by weight)
Phosphorylated polyol	–	51
Daltocel F435	51	–
Daltolac R535	30	30
Methyl propyl diol	11	11
TEP	3	3
BYK A530	0.5	0.5
Sylosiv A3	4	4
Suprasec 2237	116	116
Index	107	107

Forty grams of pre-polymer were prepared in bulk according to Table 1, except pMDI (polymeric methane diphenyl diisocyanate). The pre-polymer was first well mixed in a plastic beaker. After that, the pMDI was added into the beaker. Then, they were introduced into a round-bottomed flask equipped with a mechanical stirrer (300 rpm) and a vacuum connector for 3 min. The coatings were then put in an oven on metal plate for 60 min at 80 °C in order to complete the polymerization reactions.

The terminology used to identify samples is expressed as PGP (refers to the phosphorylated polyols) and PU GP (refers to the coating). For example, PU GP1 means a coating with a PGP1 polyol.

2.3. Characterization

Gel permeation chromatography (GPC) was used to determine the molecular weight distribution of the polymers. Measurements were performed with a Viscotek chromatography with two columns (Styragel HR2 and Styragel HR0.5) at 35 °C with a flow of 1 ml/min and THF as eluent. The calibration curves for GPC analysis were obtained with poly(ethylene glycol) standards (from Waters).

The phosphorus content in the polyol was measured by inductively coupled plasma emission spectroscopy (ICP spectroscopy) with a VARIAN 710-ES ICP Optical Emission Spectrometer, at a wavelength of 213.618 nm, using xylene as a solvent.

Hydroxyl value was measured by automatic titration in a METROHM 721 Net Titrino according to ASTM D4274-88. The hydroxyl number was determined by titration with a NaOH solution, with samples previously treated with phthalic anhydride, pyridine and imidazole at 100 °C.

Infrared spectra were recorded on a Varian 640-IR Fourier Transform IR spectrophotometer with 16 scans per experiment at a resolution of 8 cm^{-1} in the range 4000–400 cm^{-1}.

Thermogravimetric analysis (TGA) was performed with a TA instruments SDT Q600 Simultaneous DSC–TGA from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen and air atmospheres.

The analysis of the gas products distribution was carried out in a thermogravimetric analyser (TGA-DSC 1; METTLER TOLEDO)

Table 2
The main properties of phosphorylated polyether polyols.

Polyol	M_w (g/mol)	PI	P (%)	OH_v (mgKOH/g)
PGP1	1766	1.26	1.44	123
PGP2	1950	1.45	1.42	126
PGP3	2044	1.37	1.05	126
PGP4	2026	1.37	0.86	94
PGP5	2715	1.69	0.71	90
PREF	1923	1	0	56