Synthesis and characterization of phosphorus-containing, silicone rubber based flame retardant coatings

R. Januszewski[a], M. Dutkiewicz[b,c,*], H. Maciejewski[a,c], B. Marciniec[b]

[a] Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland
[b] Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89c, 61-614 Poznań, Poland
[c] Adam Mickiewicz University Foundation, Rubież 46, 61-612 Poznań, Poland

ARTICLE INFO

ABSTRACT

The synthesis and characterization of two biphenyl phosphates of different structures, as substrates for preparation of two series of functionalized addition silicone rubbers of different crosslink density and amount of pendant functional groups, is presented. Obtained materials were applied as flame retardant protective coatings for cotton fabric and characterized by TG and MMC techniques. The relationship between thermal stability, flame-retardant properties, and structure of prepared silicone rubbers is discussed.

1. Introduction

Coatings are defined as materials that are applied to cover the surface of an object to impart specific properties and for protection of various classes of materials [1]. They can be employed to prevent degradation of metals and alloys by corrosion [2], to reduce flammability [3] or to change the surface properties [4].

In recent years the synthesis and utilization of polymer-based coatings have been a focus of growing interest. Commonly, polymeric protective coatings are prepared using inter alia polyurethanes [5], polybutadienes [6], polyphosphazenes [7] or polysiloxanes [8]. Of the above examples, the siloxanes seem to be the most attractive starting reagents, because of their special properties resulting from the nature of their backbone. Polysiloxanes are known as materials characterized by low glass transition temperature ($T_g < -120\,°C$), good dielectric properties and relatively low free surface energy values. Moreover, because of the high dissociation energy of Si−O bonds (ca. 460 kJ/mol) in comparison with typical organic bonds C−O (ca. 350 kJ/mol) or C−C (ca. 340 kJ/mol). Polymeric siloxanes are commonly known to be more thermally, hydrolytically and chemically resistant materials than typical organic polymers containing aforementioned C−O and C−C bonds [9–12]. On the other hand, silicone compounds bearing Si−H Si−OH or Si−CH=CH₂ groups exhibit high reactivity in a wide range of catalytic and stoichiometric reactions, which gives an opportunity to incorporation in a wide spectrum of functional groups. Several catalytic processes can be used for siloxane functionalization like metathesis [13], silylative coupling [14], substitution [15], hydrosilylation [16],

condensation [17]. However, hydrosilylation seems to be still the most convenient and the most often used protocol for obtaining the new organosilicon compounds, thanks to its high selectivity and tolerance of functional groups such as epoxy, fluoroalkyl, chloroalkyl, tertiary amine, hydroxyl etc. [16,18]. This reaction is widely used in the synthesis of functional organosilanes, siloxanes, and polysiloxanes, as well as, for crosslinking of silicone fluids [16,19]. Functionalized polysiloxanes were applied as anti-corrosive [20], antifungal [21], highly hydrophobic [4], self-cleaning [22] or flame retardant (FR) coatings [23].

Traditionally, FRs were based on halogenated organic compounds. However, the presence of the chlorine and bromine atoms results in the production of poisonous, corrosive and toxic smoke during degradation or combustion of material [24–26]. Consequently, there is a demand for finding the environmental friendly halogen-free flame retardants to protect the human health and ecosystem [27]. The common halogen-free FRs include inter alia boron atoms [28], molecular [29] and polymeric phosphorous compounds [30] and organosilicon derivatives, such as silanes and mentioned above polysiloxanes [31]. The phosphorus-based FRs are among the most effective combustion inhibitors and can volatilize into the gas phase, to form active radicals and act as scavengers of H˙ and OH˙ radicals [32]. In the view of literature data, there is a lot of articles describing phosphorous [33–36] and silicon-based FRs [37–40], but there are only a few reports on protective coatings employing both types of compounds [41–43]. Moreover, there are no literature reports about the synthesis and the thermal behavior of well-defined polysiloxanes containing side phosphate groups.

In this paper, we presented a synthesis of two series of poly-dimethylsiloxanes functionalized with different amounts of two new biphenyl phosphates, via hydrosilylation reaction, and subsequently crosslinked with 1,1,3,3-teramethyldivinyldisiloxane in presence of Pt (0) complex. Obtained materials were applied as flame retardant coatings to cotton fabric. Hence, the goal of this work was to investigate the relationship between the amount of phosphorus and the structure of pendant groups in siloxane matrix on the thermal stability and flame retardant properties of synthesized materials.

2. Experimental

2.1. Materials

Triethylamine, allyl alcohol, phosphorus (V) oxychloride, 1,1,3,3-tetramethyldivinyldisiloxane, Karstedt's complex were obtained from Sigma-Aldrich. Eugenol and 2,2′-biphenol were purchased from Acros Organics. Poly(dimethyl-*co*-hydromethyl)siloxane was purchased from Gelest. Solvents were obtained from POCH and Sigma-Aldrich. All chemicals were used without any further purification. The 100% bleached cotton fabric of 145 g/m^2 surface weight was used in flammability tests.

2.2. Techniques

2.2.1. NMR spectroscopy

^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a Varian XL 300 spectrometer at room temperature using CDCl$_3$ as a solvent.

2.2.2. Infrared spectroscopy

FT-IR spectra were recorded using Bruker Tensor 27 Fourier transform spectrometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases, 16 scans at a resolution of 2 cm^{-1} were collected for a spectrum.

2.2.3. Mass spectrometry

MS spectra were obtained using Bruker 320-MS GC Quadrupole Mass Spectrometer with an electron impact, direct exposure probe mass spectrometry (EI/DEP/MS) technique applied.

2.2.4. Microscale combustion calorimetry (MCC)

The flammability was assessed with Pyrolysis-Combustion Flow Calorimetry (PCFC) technique. All analyses were performed using Fire Testing Technology Ltd., FAA Micro Calorimeter. The heating rate (β) was 1°Cs^{-1}, the pyrolysis temperature range 75–750 °C and the combustion temperature 900 °C. The gas flow was a mixture of O$_2$/N$_2$ 20/80 cm^3 min^{-1} and the sample weight 5–6 $\pm$ 0.01 mg. The heat release temperature (T$_{max}$), maximum specific heat release rate (Q$_{max}$) and the heat release capacity (η$_c$) were derived from the calorimetric measurements. THR parameters were calculated from the total area under the HRR curves. The tests were repeated three times and the experimental error on HRR was ± 2% and the instrumental error on T was 1 °C and t was 1 s.

2.2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a TA Instruments analyzer model TG Q50. The measurements were conducted in the air or nitrogen atmosphere (gas flow of 60 mL/min), from ambient temperature to 800 °C at the heating rate of 10 °C/min.

2.3. Fabric modification

The modification of cotton fabrics was performed by one-step method via chemical treatment with 10% premix solutions of substrates in toluene. Cotton fabrics (10 × 10 cm) were placed into a flask with a solution of reagents and stirred at room temperature for 5 min. Then

samples were removed and dried at 120 °C to constant weight. The add-on values A(%) were calculated as follows:

$$A(\%) = (W_2 - W_1)/W_1 \times 100\%$$

Where (W$_1$) stands for the weight of a fabric sample before and (W$_2$) after modification.

The flammability of obtained modified fabrics samples has been verified with PCFC technique.

2.4. Syntheses

2.4.1. Synthesis of (2,2′-biphenyldioxy)chlorophosphine oxide (1)

2,2′-biphenol (42.49 g, 228.24 mmol) in 50 mL of anhydrous THF was added to a cooled to 0 °C solution of POCl$_3$ (35 g, 228.24 mmol) in 180 mL of anhydrous toluene. Then to obtained mixture triethylamine (46.2 g, 456.4 mmol) was added dropwise. The reaction was monitored by FT-IR spectroscopy by observing changes in the area of the bands assigned to the hydroxyl group and P−Cl bond. After the reaction, formed precipitate was filtered off and washed with cold toluene. Evaporation of the solvent gave pure product as a white powder with a 96.5% yield. ^{1}H NMR (CDCl$_3$, δ (ppm)): 7.60–7.58 CH$_{arom.}$, (m, 2H), 7.52–7.48 CH$_{arom.}$, (m, 2H), 7.46–7.42 CH$_{arom.}$, (m, 2H), 7.37–7.35 CH$_{arom.}$, (m, 2H). ^{13}C NMR (CDCl$_3$, δ (ppm)): 147.54C−O, 130.48C−C, 130.17 CH, 128.14C−C=CH, 127.34 CH, 121.45 O−C=CH. ^{31}P NMR (CDCl$_3$, δ (ppm)): 9.87. DEP-MS 70 eV (*m/z*): 266.0 (M), 168.0 (M - ClO$_2$P^{2+}). FT-IR ATR (cm^{-1}): 3070.77C−H$_{arom.}$ Str.; 1604.46, 1498.80, 1474.37, 1433.65C=C$_{arom.}$ str., 1296.65 P=O str.; 1244.00, 1187.22, 1170.89, 1092.59, 924.41 P−O−C str.; 782.51, 713.73, 613.36, 521.99 P−O−C str.; 751.77C−H ben.; 561.13 P−Cl str.

2.4.2. Synthesis of allyloxy(2,2′-biphenyldioxy)phosphine oxide (2) - AllBPh

Allyl alcohol (5.5 g, 93.75 mmol) was added dropwise to a cooled to 0 °C solution of (1) (25 g, 93.75 mmol) and triethylamine (10.75 g, 103.13 mmol) in 125 mL of THF. The reaction was monitored by FT-IR spectroscopy by observing changes in the area of the band assigned to the P−Cl bond. After the reaction formed precipitate was filtered off and washed with cold THF. Evaporation of the solvent gave a pure product with a 95% yield. ^{1}H NMR (CDCl$_3$, δ (ppm)): 7.53–7.28 CH$_{arom.}$, (m, 8H), 6.98 −CH=CH$_2$ (m, 1H), 5.42–5.38, 5.32–5.29 −CH=CH$_2$ (dd, 2H), 4.80–4.77 −O−CH$_2$−CH (m, 2H). ^{13}C NMR (CDCl$_3$, δ (ppm)): 147.89 O−C=CH, 131.87 −CH=CH$_2$, 130.16C−C−CH, 129.99C−C, 128.31 CH$_{arom.}$, 126.59 CH$_{arom.}$, 121.46 CH$_{arom.}$, 119.31 −CH=CH$_2$, 69.93 O−CH$_2$−CH. ^{31}P NMR (CDCl$_3$, δ (ppm)): 1.70. DEP-MS 70 eV (*m/z*): 288.1 (M), 247.0 (M - C$_3$H$_5$˙), 232.1 ([M + H] - C$_3$H$_5$O), 168.0 (M - C$_3$H$_5$O$_3$P˙). FT-IR ATR (cm^{-1}): 3066.20C−H $_{arom.}$ str.; 2985.37C−H$_{alkyl}$ str.; 1652.10C=C$_{alkene}$; 1604.47, 1499.39, 1476.71, 1435.90C=C$_{arom.}$ str., 1298.63 P=O str.; 1248.60, 1205.57, 1185.66, 1091.13, 1014.06, 931.44 P−O−C str.; 788.44, 717.00, 609.32, 523.86 P−O−C str.; 756.11C−H ben.

2.4.3. Synthesis of (2,2′-biphenyldioxy)(2-methoxy-4-allylphenoxy) phosphine oxide (3) - PheBPh

4-allyl-2-methoxyphenol (15.4 g, 93.75 mmol) was added dropwise to a cooled to 0 °C solution of (1) (25 g, 93.75 mmol) and triethylamine (10.75 g, 103.13 mmol) in 125 mL of THF. The reaction was monitored by FT-IR spectroscopy by observing changes in the area of the bands assigned to the hydroxyl group and P−Cl bond. After the reaction formed precipitate was filtered off and washed with cold THF. Evaporation of the solvent gave the product with 96% yield. ^{1}H NMR (CDCl$_3$, δ (ppm)): 7.54–7.26 CH$_{arom.}$ (m, 8H), 6.86–6.69 CH$_{eugenol}$ (m, 3H), 5.95 −CH=CH$_2$ (m, 1H), 5.09 −CH=CH$_2$ (m, 2H), 3.88 O−CH$_3$ (s, 3H), 3.36C−CH$_2$−CH=(d, 2H). ^{13}C NMR (CDCl$_3$, δ (ppm)): 150.37 CH$_3$−O−C$_{eugenol}$, 147.87 P−O−C$_{phenyl}$, 138.71 P−O−C$_{eugenol}$, 138.13 CH$_2$−CH−C$_{eugenol}$, 137.01 CH$_2$=CH−CH$_2$, 130.09C−C−CH$_{phenyl}$, 129.92C−C$_{phenyl}$, 128.32 CH$_{phenyl}$, 126.61 CH$_{phenyl}$, 121.65 CH$_{phenyl}$,