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The effects of triphenylphosphate and recorcinolbis(diphenylphosphate) on the thermal degradation of polycarbonate in air

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Abstract

The thermal degradation of polycarbonate/triphenylphosphate (PC/TPP) and PC/resocinolbis(diphenylphosphate) (PC/RDP) in air has been studied using TGA/FTIR and GC/MS. In PC/phosphate blends, the phosphate stabilizes the carbonate group of polycarbonate from alcoholysis between the alcohol products of polycarbonate degradation and the carbonate linkage. Thus, the evolution of bisphenol A, which is mainly produced via hydrolysis/alcoholysis of the carbonate linkage, is significantly reduced, while, the evolution of various alkylphenols and diarylcarbonates increases. The bonds that are broken first in the thermal degradation of both the carbonate and isopropylidene linkages of polycarbonate are the weakest bonds in each, when a phosphate is present. Triphenylphosphate and resocinolbis(diphenyl-phosphate), even though they exhibit a significant difference in their volatilization temperature, appear to play a similar role in the degradation pathway of polycarbonate.

Keywords: Polycarbonate; Thermal degradation; Fire retardancy; Triphenylphosphate; Resorcinoldiphosphate

1. Introduction

Since the environmental issues of halogen compounds were raised in the 1980s, halogen fire retardants have been voluntarily phased out, especially in the European market, and non-halogenated fire retardant systems have been very actively studied and used [1,2]. Among non-halogenated fire retardants, aryl-phosphates are representative, because they are generally thermally stable and exhibit good plasticization and compatibility with many polymers. However, there are only a few non-halogenated fire retardant polymer systems using aryl-phosphates as flame retardants [2–4].

The aryl-phosphates include monophosphates, such as triphenylphosphate (TPP), tricresylphosphate, cresyldiphenyl phosphate, trixylylphosphate, etc., and bisphosphates including resorcinol bis(diphenylphosphate) (RDP), bisphenol A bis(diphenylphosphate), etc. Both condensed phase and vapor phase fire retardant effects have been suggested as the modes of action for the aryl-phosphates [5–8]. The vapor phase fire retardation effect is considered to be identical to the radical trap mechanism of halogen compounds, capturing the hydrogen and hydroxy radicals which contribute to combustion reactions [11]. The condensed phase mechanisms are mainly explained by coating and charring. Regarding the coating mechanism, it was suggested that phosphorus compounds could migrate to the surface, decompose to phosphoric acid and these acids could form a molten viscous surface layer protecting the polymer substrate from flame and oxygen [14]. For the charring mechanism, it was felt that aryl-phosphates promote and enhance char formation.

Among aryl-phosphates, TPP and RDP are very good examples for the study of degradation mechanisms, since they have relatively simple structures and show significantly different thermal mass loss behavior. Shank and coworkers studied the flame retardant mechanism for phosphorus flame retardancy of TPP in PPO/HIPS and suggested a predominantly vapor phase mechanism [9]. Levchik and coworkers studied the thermal degradation of PPO/HIPS/RDP and PC/ABS/RDP using TGA and FTIR and proposed that RDP chemically reacts with PPO or PC and the fire retardant action is mainly a condensed phase mechanism [10–12]. Al-

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though the fire retardant mechanisms of aryl-phosphates in the condensed phase were proposed in the above work, the mechanism of fire retardation by phosphorus compounds has not been elucidated in terms of reactions which occur and the products that result.

An accurate understanding of the mechanism of fire retardancy with a given polymer is very important in the design of more effective fire retardant systems and the fire retardant action is closely related to the degradation behavior of the polymer. In order to elucidate the fire retardant action of aryl-phosphates in polymer/aryl-phosphate blends, an understanding of the degradation pathway of the polymer is necessary.

Polycarbonate (PC) is one of good char forming polymers and polycarbonate and its blend with acrylonitrile–butadiene–styrene (ABS) using aryl-phosphate fire retardants are widely used in electrical appliances. Polycarbonate exhibits excellent mechanical properties and a high limiting oxygen index (LOI) value of 27 and produces a large fraction of char upon combustion [13]. Thus, the thermal degradation of polycarbonate has been the subject of a number of studies. Lee [14] and McNeill and Rincon [15,16] suggested homolytic chain scission mechanisms on the thermal degradation of PC. Davis and Golden proposed the Kolbe–Schmitt rearrangement of carbonate linkage for the formation of xanthone structure [17,18]. Montaudo and co-workers assigned xanthone units as one of main evolved functional group and proposed that the major degradation pathway for PC is ester exchange of the carbonate linkage and disproportionation of isopropylidene linkage [19–24]. They also analyzed the THF-soluble fraction of thermally oxidized PC at 300 and 350 °C, and suggested that the oxidation pathway begins with radical formation in the isopropylidene linkage through hydrogen cleavage, followed by subsequent rearrangement and peroxide formation [25].

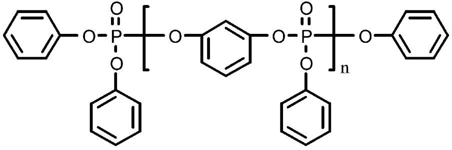
However, the environment of a decomposing sample may affect the degradation pathways. For instance, the degradation behavior upon heating and/or combustion may be altered in the presence of oxygen and the pressure during decomposition affects the composition of the evolved products. Since the above results were mostly acquired under vacuum or in an inert atmosphere, there are still some aspects of the degradation behavior during burning of polymers which require further elucidation. In this laboratory, TGA was used to study the thermal degradation of PC in nitrogen and air, to obtain information at atmospheric pressure as well as under real combustion conditions, and the significant evolved products were assigned using FTIR, GC/MS and LC/MS. It was proposed that the evolved products are produced mainly by chain scission of the isopropylidene linkage and hydrolysis/alcoholysis of the carbonate linkage, and that the presence of oxygen primarily affects only the beginning stage of degradation [26,27].

In order to determine the effect of typical fire retardants on the degradation of polycarbonate, TPP and RDP were blended with PC at 12 wt.%, which is sufficient to obtain a UL94 V-0 rating [10,11]. Since the burning of polymers is a very complicated thermal process and the heat and mass transfer through the burning surface of polymer substrate causes a large temperature gradient in the interior of the polymer, flash pyrolysis as well as gradual pyrolysis has been carried out using TGA in air to simulate real combustion. For the molecular structure identification, the evolved volatile products were analyzed using in situ vapor phase FTIR and the volatiles were also collected under each pyrolysis condition for further analysis using FTIR and GC/MS. The solid residues after pyrolysis were analyzed using FTIR.

2. Experimental

2.1. Materials

The polycarbonate sample was provided by Cheil Industries Inc., and was used as received; this material is end-capped with *t*-butyl phenol for enhanced thermal stability. The number and weight average molecular weight of the bisphenol A polycarbonate are 16,000 and 28,000, respectively. Triphenylphosphate (TPP) and resorcinolbis(diphenylphosphate) (RDP) were provided by Akzo Nobel and were also used as received. TPP is a white flake solid with a melting point of 48 °C, while, RDP contains 65% dimer ($n = 1$), 30% higher oligomers ($n \geq 2$) and up to 5% of TPP ($n = 0$), as shown below.



2.2. Sample preparation

Polycarbonate and TPP or RDP were melt-blended in a Brabender Mixer for 5 min at 250 °C with 12 wt.% of phosphate in the total composition.

2.3. TGA/FTIR analysis

TGA/FTIR was carried out on a Cahn TG 131 instrument which was connected to a Mattson Research grade FTIR through stainless steel tubing. The temperature reproducibility of the TGA is ±3 °C and error range of nonvolatile fraction at 700 °C is ±3%. The thermal degradation in TGA was carried out under an air flow of 80 ml/min. The sample size was 40–60 mg for the TGA evaluation. During thermal degradation in TGA, the evolved volatile products are introduced to the IR chamber through a sniffer tube and stainless steel tubing, and in situ vapor phase FTIR spectra are collected; this sniffer tube extends into the sample cup in TGA and removes the evolved products at the rate of 40 ml/min. The temperature of the tubing was 300 °C.