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Kinetics of thermal degradation of intumescent flame-retardant spirophosphates

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Abstract. The thermal degradation behaviour of various spirophosphates synthesized using SDP (phenol), SDOC (*o*-cresol), SDMC (*m*-cresol), SDPC (*p*-cresol), SDDMP (2,4-dimethylphenol) and SDTMP (2,4,6-trimethylphenol) with 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide (SDCDP) are investigated using thermogravimetric analyzer. The spirophosphates show multistage degradations in the temperature range 180–550°C. The second stage of degradation is more prominent and the substituent effect is clearly reflected at this stage of degradation. The compound SDP showed superior performance since it has the greatest char yield value (44%) and LOI value (27%). The model free kinetic methods of Flynn-Wall-Ozawa and Vyazovkin methods are used to calculate the apparent energy of activation for the thermal degradation (E_a-D) of these spirophosphates. The material SDTMP showed the highest E_a-D values.

Keywords. Spirophosphates; intumescence; thermogravimetric analysis; degradation kinetics; flame retardants.

1. Introduction

Polymeric materials (due to light weight, durability, mechanical performance and resistance towards chemicals, etc.) are advantageously used in many fields (household products, defence materials, aerospace parts and marine parts, etc.). However, the use of polymeric materials is restricted due to its fire risk properties [1,2]. Usually the incorporation of flame-retardant additives or the development of flame-retardant coatings for polymer is the convenient method to impart polymer flame retardancy [3,4]. At present, research has been focused on to develop environmental friendly flame-retardant systems. The patents and literature on environmental friendly flame retardants illustrated the importance of phosphorus-based flame retardants and indicated as very good alternate for halogenated flame retardants. The research on phosphorus-based flame retardants is originated with ammonium polyphosphate (APP) [5].

Phosphorus-based intumescent systems are attracted by many researchers, since it forms nonoxidizable multi-cellular charred layer in the fire condition. The formed char insulate and protect the materials of interest. The acid source, carbonific and spumific agents required to formulate the intumescent system has more than one functional group. Thus the mechanism of intumescence is complex in nature [6–9].

Previously, the authors synthesized a series of spirophosphates by reacting spirodichlorodiphosphate with phenol, *o*-cresol, *m*-cresol, *p*-cresol, 2,6-dimethylphenol and 2,4,6-trimethylphenol [10,11]. The materials were pyrolysed at 500°C for a constant period (5 s) and the volatile products evolved were analysed using GC-MS. From these results attempts were made to elucidate the degradation mechanism of spirophosphates, which will add to the present understanding of the intumescent behaviour of phosphorus-based compounds. The research carried out on various spirophosphates has been reviewed [12].

It is well known that the flame retardancy of the materials also depends on the thermal stability, degradation rate, char forming rate and char yield. Thermogravimetric (TG) analysis is one among the standard procedures to investigate the thermal stability and the degradation of a material. Getting appropriate data and calculations will provide the kinetic triplets, the apparent activation energy for thermal degradation (E_a-D), the frequency factor (A) and the reaction model $f(\alpha)$. As per the recommendations of Flynn–Wall–Ozawa (FWO) [13,14] and Vyazovkin (VYZ) [15], multiple heating

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