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Chemistry of char forming mechanism of spirophosphates

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Abstract

The spirophosphates are an important class of intumescent system, which produces effective voluminous char to protect the underlying materials. The char developed during the intumescent process play vital role in the flame retardant mechanism. Six different spirophosphates were synthesized, by treating spirodichlorodiphosphate with phenol, cresols (o-, m- and p-isomers), di- and tri-methyl phenols and their char forming chemistry were investigated. The residual char acquired by subjecting the synthesized intumescent materials to isothermal pyrolysis at 300°C, 400°C, 500°C and 600°C were investigated by FTIR and SEM analysis. FTIR analysis indicated the formation of structurally similar chemical entities from these intumescent materials when they were subjected to isothermal pyrolysis at different temperatures. The formation of phosphate rich carbonaceous complexes was identified. SEM analysis showed that the char produced was having considerably a compact structure.

Keywords: Spirophosphates, Intumescence, Char, Condensed phase mechanism, Phosphoric acids.

Introduction

Intumescent materials have been used for polymers, wood articles, metals, etc., for protection against fire due to their action in both the vapour and condensed phases. Intumescent materials on fire situation produce non-oxidizable multicellular char, which reduces the oxygen entry into the underlying substrate[1-3].

The chemistry of intumescent mechanism is difficult to understand, due to the multifunctional character of the intumescent materials, since, here dehydration of carbon rich compound is triggered by the acid molecules released during heating. Continuously and simultaneously, the spumific agent present in the intumescent system releases gaseous molecules and is responsible for the enlarged foaming action of the intumescent materials.

In few cases, the addition of intumescent materials alone has not given the required effect. Hence researchers introduced some additives as synergistic agent along with the intumescent materials to increase or to achieve the required effect. The thermal resistance and barrier properties of the char bonded structure formed during intumescence will depend on the resistance of char to oxidation, thermal insulation and mechanical resilience of char. These properties are generally determined by the physical and chemical structures of the char formed[4-11].

Few researchers have paid much attention to the chemical process takes place during intumescence and they developed several models to study the heat transfer mechanism to the underlying materials. Intumescent flame retardants are characterized by molecular structure, thermal, flame retardant properties and char studies. Each one of these analyses will give its own results about the intumescent flame retardants. The char formed during intumescence has the properties of reducing volatile mass, acting as thermal insulation, obstructing the release of combustible gases and increasing the thermal insulation capacity.

Hence it is of equal importance to study in detail the char formation mechanisms. Wang and Chen[12] study indicated that the effectiveness of flame retardancy of the material depends on the cellular char developed during intumescence. It is needed to reacts phosphorus based flame retardants with polymers to promote charring. Levchik[13] et al reviewed the phosphorus flame retardants for plastics and foams.

The addition of synergistic gents like nitrogen compounds to the phosphorus flame retardants promotes charring efficiently with noncharrable polymers[14]. The study of the char forming chemistry and both the structure and morphology of the carbon char produced during intumescence will definitely help to understand the much complex intumescent mechanism. The need of investigation of char structure and properties are clearly described by Zhang et al[15]. The most widely studied intumescent flame retardant systems are ammonium polyphosphates (APP)/pentaerythritol (PER)/melamine (MEL) and are elaborately studied by Camino et al[5,16] and Kandola et al[17]. Mechanism of char formation of biobased carbonization agent containing intumescent system was studied and reported by Maqsood et al[18]. In the present work, attempts were made to study char forming mechanism using FTIR and SEM techniques for the compounds prepared by reacting spirodichlorodi phosphate with different phenols.

Material and methods

The addition of chemicals such as, phenol, cresols (*o*-, *m*- and *p*-isomers), di- and tri- methyl phenol to the spirodichlorodi phosphates results the investigated compounds SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP respectively.

The complete synthetic procedure used was discussed effectively in the references[19-21]. The chemical structure of the compounds investigated is depicted in the Figure-1.

Techniques: The residues obtained by isothermally pyrolyzing the samples at different temperatures for constant time interval (300°C, 400°C, 500°C and 600°C for 10 min) in a muffle furnace were examined by FT-IR to determine the structural features of the char. FT-IR spectra were recorded on Fourier Transform Infrared-8400S spectrophotometer, Shimadzu, Japan using KBr pellet technique. The morphologies of the chars were observed using Hitachi, S-3400 Scanning Electron Microscope.

Results and discussion

Fourier transform infrared spectral studies: The FT-IR spectra of the chars of the investigated compounds SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP obtained at different temperatures is presented in Figure-2. The peaks at 1200, 1033 and 500cm^{-1} noted in the FT-IR spectra of char obtained from SDP by heating at 300°C for 10 min. correspond to the group vibrations of P=O, P-O-C and PO_2/PO_3 in phosphate-carbon complexes. These bands broaden and shift to lower wave number region [1155 (P=O), 1010 (P-O-C) and 493cm^{-1} (PO_2/PO_3)] for the chars obtained by heating at high temperatures (400°C, 500°C and 600°C) for 10 min. This is may be due to the formation of phosphor-carbonaceous char structures.

The progressive increase in the intensity of peak at 1643cm^{-1} (benzene nucleus) confirmed the presence and increase of aromatized units in the char during intumescence.

It is noted that all the recorded FT-IR spectra of the char materials obtained by heating the samples at 300°C, 400°C, 500°C and 600°C for 10 min. are relatively similar indicating the formation of nearly similar chemical structures. The results demonstrate that the compound SDP is able to produce phosphoric acids and polyphosphoric acids during thermal degradation, which is responsible for the formation of heat resistant carbonaceous char[22,23]. The similar observation was noted for the compounds SDOC, SDMC, SDPC, SDDMP and SDTMP.

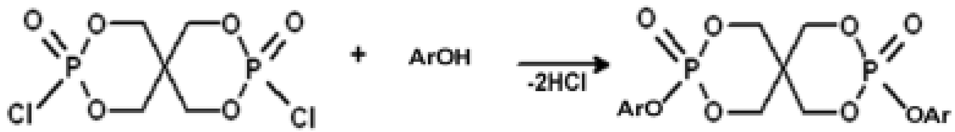
Scanning electron microscope studies: The micrographs of the char samples obtained at 300°C and 600°C from the compounds SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP were taken in 1000× magnification and presented in Figures-3 and 4 respectively.

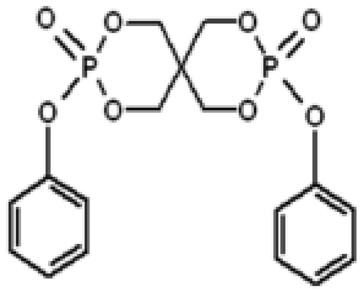
The char obtained from SDP, SDDMP and SDTMP at 300 °C showed more compact and denser surface with honeycomb bubbles on it, indicating the formation of strong char surface during the initial stage of intumescence. The char from SDOC and SDMC acquired at 300°C showed less dense surfaces. Moreover, crack was seen on the soft char surface of the compound SDPC. The reported literature[25] suggested that the caves on the char surface are mainly due to the sudden escape of gaseous decomposition products from the degrading matrix. Air convection is less when the caves are small in size whereas air convection is high if the caves are too big in size. One can find no caves on the surfaces of the chars of SDP, SDOC, SDMC, SDDMP and SDTMP obtained at 300°C which indicates the limiting transfer of gaseous decomposition products to gas phase in the compounds during degradation.

Hence heat transfer from flame to the condensed phase and oxygen diffusion to the condensed phase are not possible. But the cracks observed in the surface of the char of SDPC may be due to the allowance of the gaseous decomposition products to escape out from the degrading matrix. Hence heat transfer from the thermal feedback to the condensed phase and oxygen diffusion in the condensed phase may be possible[24].

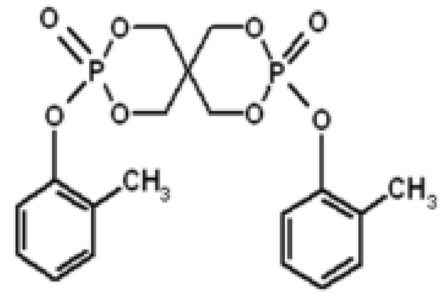
In order to form foamed multi-cellular intumescent char, successive acid formation, melting, acid attack and release of gas for blowing the char must occur almost simultaneously. The brisk formation of defensive intumescent char is mainly depending on the fire temperature and the viscosity of melt. For instance, if the viscosity of the molten material becomes very low, then large cells are formed during the blowing process and these large cells are relatively ineffective as insulator and the char can become quite frangible. Early release of gas from the blowing agent leads to poor intumescence. If the release of gas occurs too late then the char solidifies and inhibits intumescence.

The char obtained from the samples SDP and SDMC at higher temperature (600°C/10min.) showed the presence of informal open cellular cells that means big broken cells with a thick skin on the surface of char. So, they are less effective to block the heat transfer from thermal feedback and oxygen diffusion from the external sources to substrate and mass transfer from the substrate to gas phase. On the other hand, the chars of SDOC, SDPC, SDDMP and SDTMP acquired at 600°C/10 min. showed much compact regular structures with thick skins and are effective insulators[24].

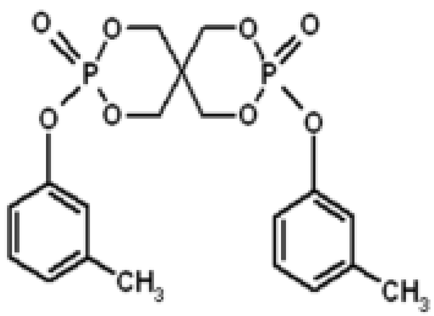




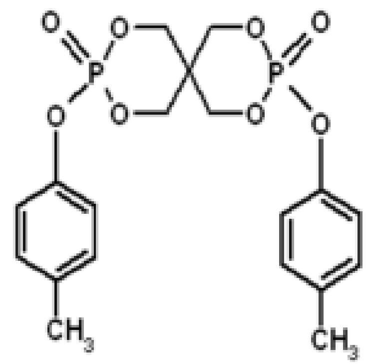
Spiro diphenyl diphosphate (SDP)



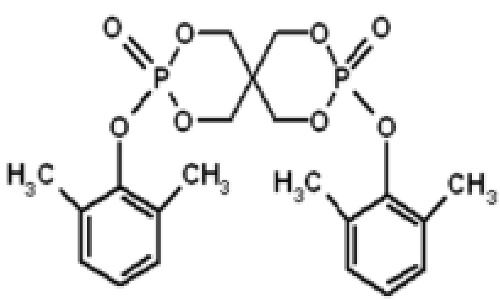
Spiro di(*o*-cresyl) diphosphate (SDOC)



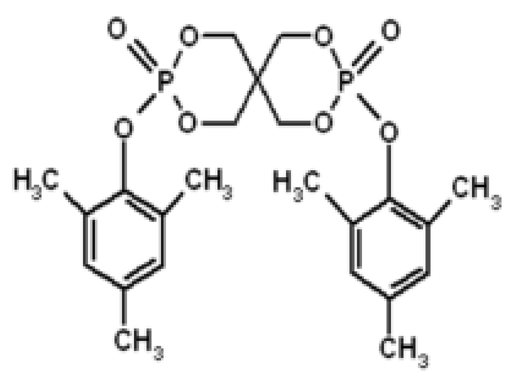
Spiro di(*m*-cresyl) diphosphate (SDMC)



Spiro di(*p*–cresyl) diphosphate (SDPC)



Spiro di(2,6-dimethylphenol) diphosphate (SDDMP)



Spiro di(2,4,6-trimethylphenol) diphosphate (SDTMP)

Figure-1: Molecular composition structures of spirophosphates.

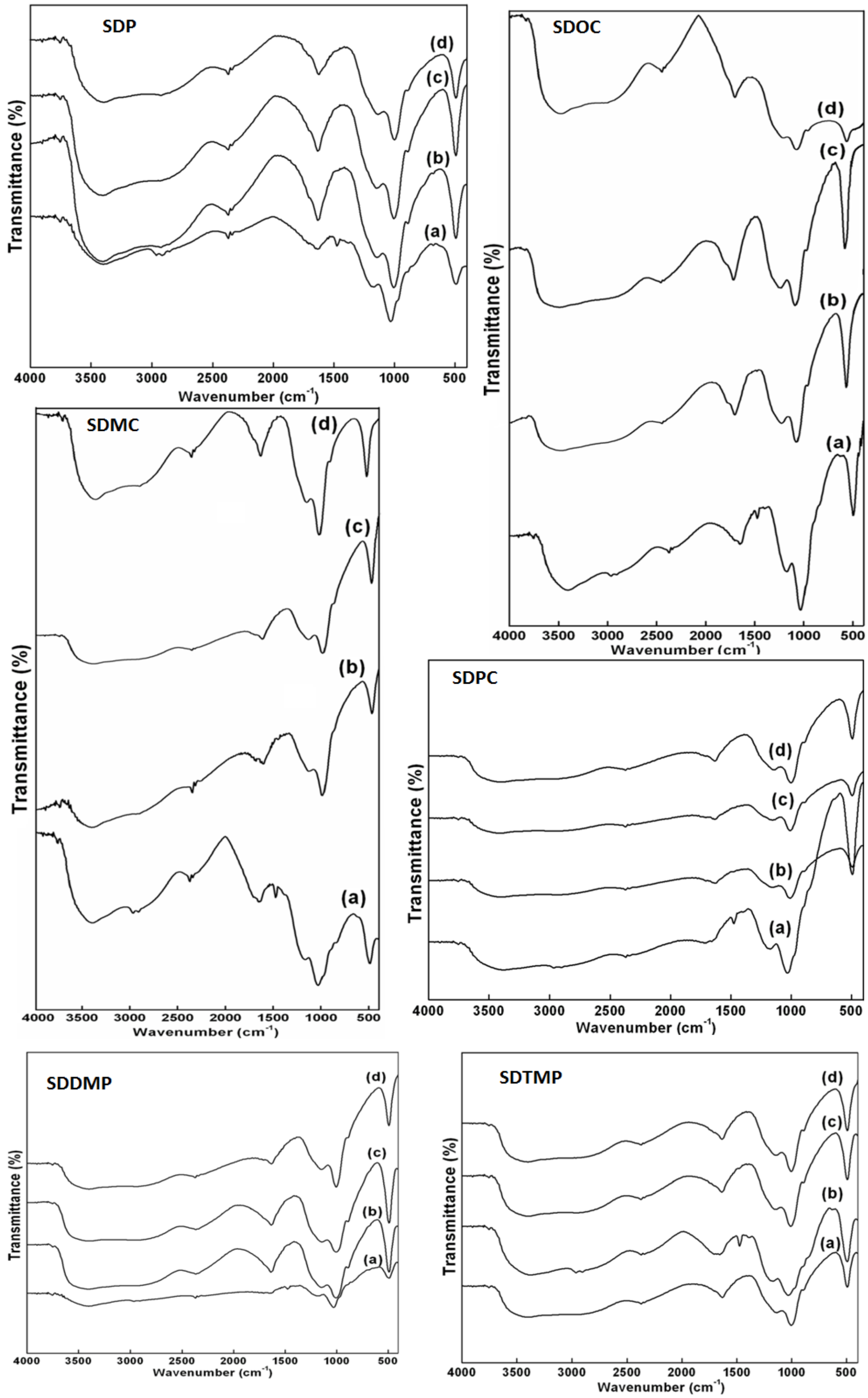


Figure-2: FT-IR spectra of char materials obtained from the spirophosphates investigated by heating at (a) 300°C, (b) 400°C, (c) 500°C and (d) 600°C for 10 min.

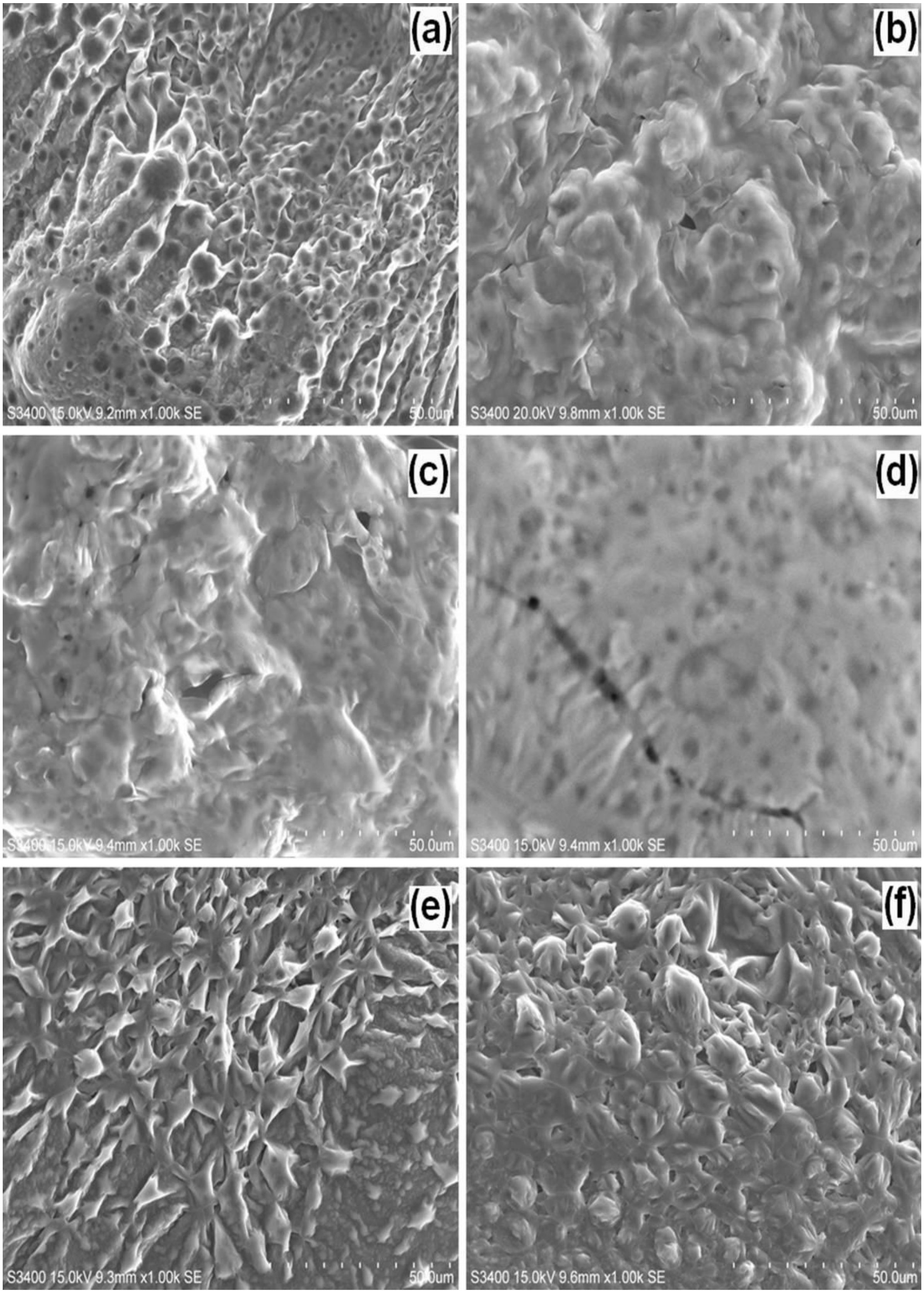


Figure-3: SEM images of the char samples obtained from (a) SDP, (b) SDOC, (c) SDMC, (d) SDPC, (e) SDDMP and (f) SDTMP at 300°C for 10min.

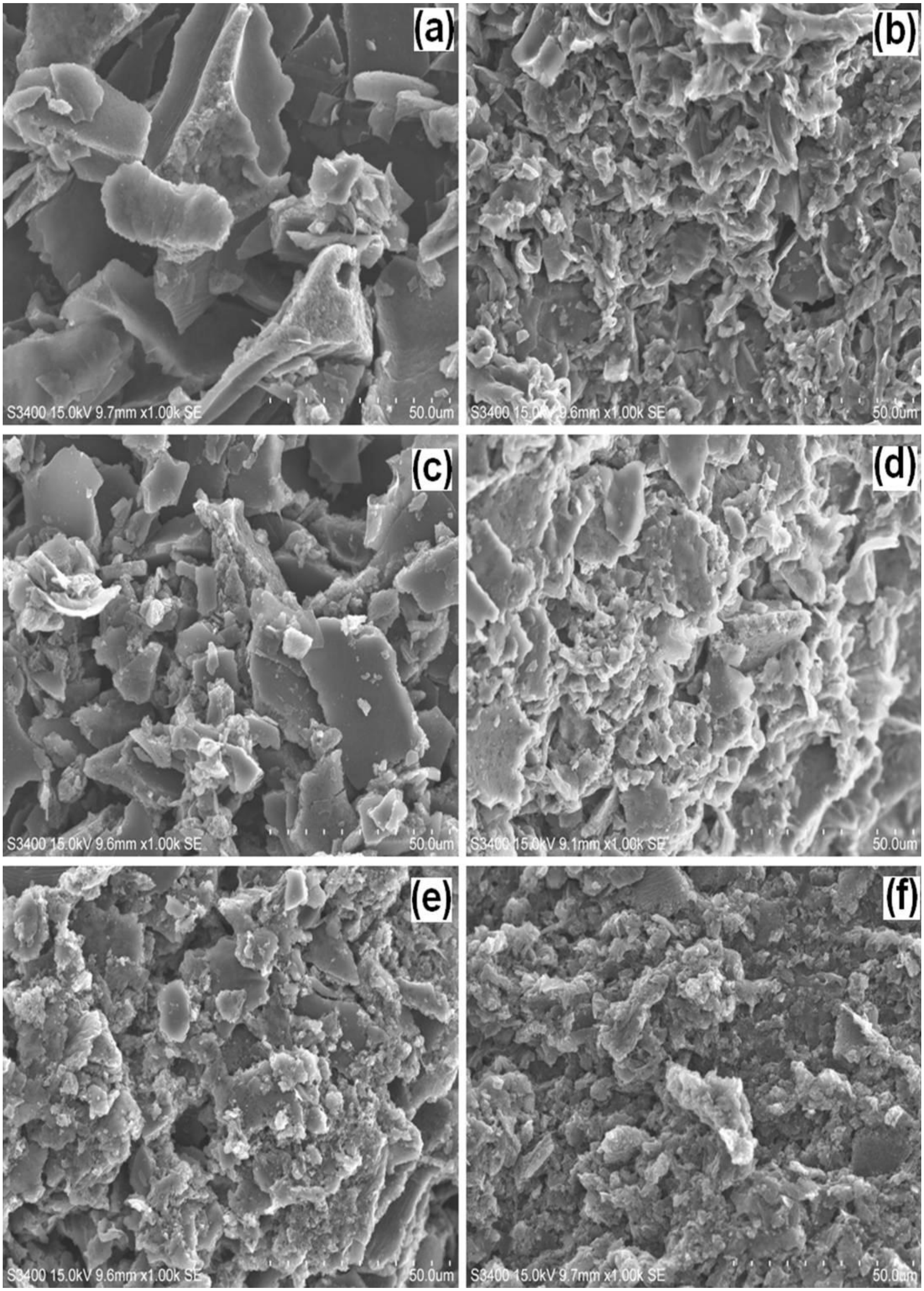


Figure-4: SEM images of the char samples obtained from (a) SDP, (b) SDOC, (c) SDMC, (d) SDPC, (e) SDDMP and (f) SDTMP at 600°C for 10 min.

Conclusion

Fourier transform infrared spectral studies of the char residues formed at different temperatures for constant time intervals from all the spirophosphates investigated showed same pattern of spectra and confirms the formation of phosphoric and polyphosphoric acids during intumescence which triggered the phospho-carbonaceous (P-O-C) char formation. At higher temperatures, the formations of informal open cellular char structures with thick skin on the surface restrict the heat and mass transfer. The char of SDOC, SDPC, SDDMP and SDTMP acquired at 600°C showed compact regular structures with thick skin, and are noted as effective insulator. This study clearly illustrated that the compounds SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP can be incorporated to polymers, wood, metals, etc., to acquire better intumescent flame retarding action.

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