Synthesis and Characterization of Phosphorus Containing N-Heterocyclic Functionalised Poly (Vinylalcohol) with Enhanced Flame Retardancy and Biological Activity

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Abstract- Functional modification of PVA or introducing reactive functional groups into the polymer chain has been believed to have basic significance while expanding its application. Phosphorous containing nitrogen heterocyclic compounds have been synthesized. The synthesized compounds were characterized using FTIR, NMR spectral studies. Thermo gravimetric analysis (TGA) display that organophosphorous-N-heterocyclic modified PVA has thermally more stable than that of unmodified PVA. Morphological and XRD have also been carried out to notify the surface morphology and amorphous nature of the organophosphorous N-heterocyclic modified polymers. The results of antibacterial activity among the modified and unmodified PVA have been compared. In general, heterocyclic modified PVA has superior in overall properties viz., thermal stability, organosolubility, flame retardancy, biological activity than that of pure PVA.

Keywords: Heterocyclic functionallized vinyl PVA, flame retardancy, thermal stability, and biological activity.

I. INTRODUCTION

Poly (vinyl alcohol) (PVA) is a nontoxic, water-soluble, biocompatible and biodegradable polymer, which is widely employed in various applications such as fibers for textile industries, films, membranes, materials for drug delivery system and cancer cell-killing embolic materials [1]. PVA fibers, gels and films are potentially high performance materials because they have high tensile strength and modulus, excellent impact strength, high abrasion resistance, excellent alkali resistance and oxygen barrier property [2].

Functional modification of PVA or introducing reactive functional groups into the polymer chain has been believed to have basic significance while expanding its application. Many researchers have reported about the modification of polymer for the purpose of introducing carboxylic, sulfonate and amino groups [3, 4] for specific applications.Heterocycles, the largest classical division of organic chemistry, found to have immense biologically and industrially important one. Heterocyclic chemistry is a branch which is inseparable from mankind because human are totally dependent on the drugs derives from heterocyclic rings. Imidazoles play an important role in life process and many imidazoles are known to form part of vitamins, enzymes and many pharmacologically important drugs. Imidazoles are probably the most well-known heterocycle, which is common and important feature of a variety of natural products and medicinal agents. Derivatives of imidazole were reported for anti-inflammatory [1-4], analgesic [5], anticonvulsant [6,7]tuberculostatic[8], antimicrobial [9] and anticancer [10] activities. Synthesis of PVA that contains phosphorus and heteroaromatics in the polymer chain attracted the attention of many researchers due to their peculiar characteristics viz, non-flammability, thermal stability, high melting points, appreciable biological activities [11 -12].

Hence, the scope of the present investigation was aimed to synthesize organophosphorus nitrogen heterocyclic functionalised poly (vinyl alcohol) and characterized for their efficiency in biological activity.

II. EXPERIMENTAL

A. Materials

Poly(vinyl alcohol) (PVA) (MW=14000) with a degree of hydrolysis of 98-99% and phosphorus oxychloride was supplied by SD Fine Chemicals, India, benzimidazole and Tetrahydrofuran were purchased from Sigma-Aldrich, Mumbai, India. Organic solvents like DMF have been received as analytical grade from Avra synthesis, Hyderabad, India. The solvents were purified according to the standard procedure. Triethylamine was also obtained from Avra synthesis, Hyderabad, Indi

Synthesis of benzimidazole-1H-1-phosphonyl dichloride

Benzimidazole (0.68 g, 10 mmol) and phosphorus oxy chloride (0.93ml, 10 mmol) were dissolved separately in 20ml of dry THF each and added slowly one over the other using dropping funnel with constant stirring for 30min at 0ºC in the presence of catalytic amount of triethylamine under the inert atmosphere. The reaction

has been carried out for 4 hrs. Then the reaction mixture was filtered, and the solvent was evaporated to get benzimidazole-1H-1-phosphonyl dichloride.The progress of the reaction was monitored by TLC and purified by column chromatography using ethyl acetate: hexane (9:1)[13]

Poly (divinyl benzimidazol-1H-yl-1-phosphonate)

The synthetic procedure for the modification of PVA was followed from our early literature report [13]. In a 250 ml three necked round bottom flask, 6 mol of PVA was dissolved in 50 ml of DMF and 1 molar ratio of triethylamine was added under inert atmosphere. Then, 1 molar ratio of 1H-benzimidazole-1-phosphonyl dichloride in 50 ml DMF was added drop wise to the reaction flask and maintained the temperature at 90^{o}C for 12 hours with constant stirring. A white triethylaminehydrochloride was removed from the reaction mixture by filtration. Then the solvent was removed under reduced pressure and the resulting product was dried at 60^{o}C using vacuum oven furnished light brown waxy polymer (Yield: 85 %). This was soluble in DMSO.

III. RESULTS AND DISCUSSION

1H-benzimidazole-1-phosphonyl dichloride

FTIR (KBr, cm^{-1}): 2952 (aromatic CH stretching), 1251 (P=O), 1074 (P-N). ^{1}H NMR DMSO-d_6, ppm): 6.9 (s, 1H), 7.2 (d, 2H), 7.4 (s, 1H) and 7.7 (s, 1H).^{31}P NMR DMSO-d_6, ppm): -1.98

Poly (divinyl benzimidazol-1-yl-1-phosphonate)

FTIR (KBr, cm^{-1}): 3284 (OH), 2911 (aromatic CH), 1426 (P-Ph), 1244 (P=O), 1137 (P-N), 1086 (P-O-C). ^{13}C NMR (DMSO-d_6, ppm): 115-162 (benzimidazole carbons), 66- 68 (P-O-CH-), 45 (OH-CH_2), 30 (CH_2).

FTIR information of phosphorus- containing N-heterocyclic modified PVA at 3284 2911 (aromatic CH stretching), 1244 (P=O), 1137 (N-P), 1086 (P-O.C), stretching values confirms the formation of the product. From the ^{13}C NMR spectrum at 115,123,138,137,162,66,67,45 and 30 ppm corresponds to aromatic carbon, benzimidazole carbon, aliphatic CH carbon and aliphatic CH_2 carbon respectively.

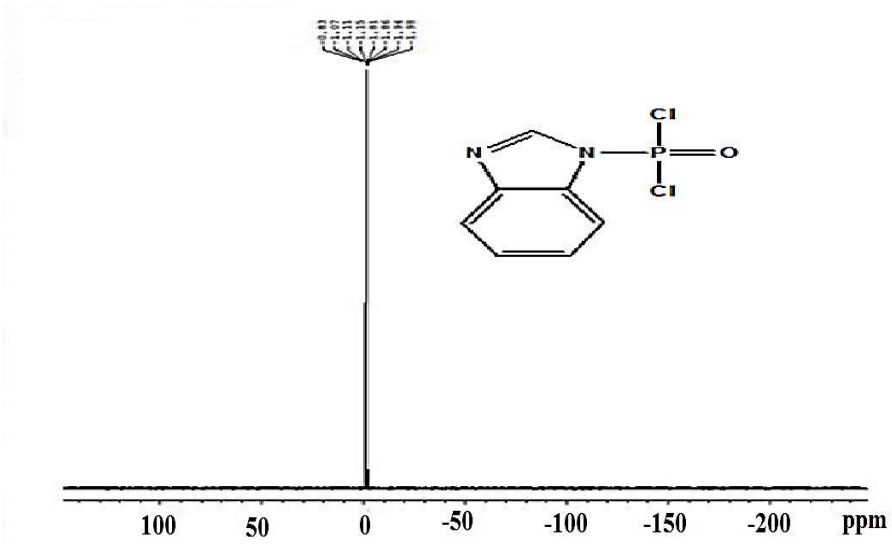

Fig.1b of ^{31}P of benzimidazole-1H-1-phosphonyl dichloride

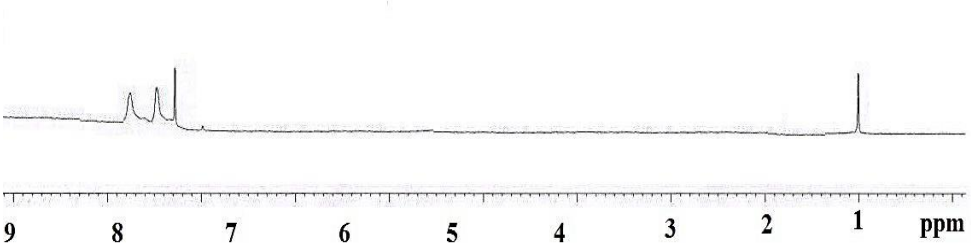

Fig.1a of ^{1}H NMR of benzimidazole -1H-1-phosphonyl dichloride

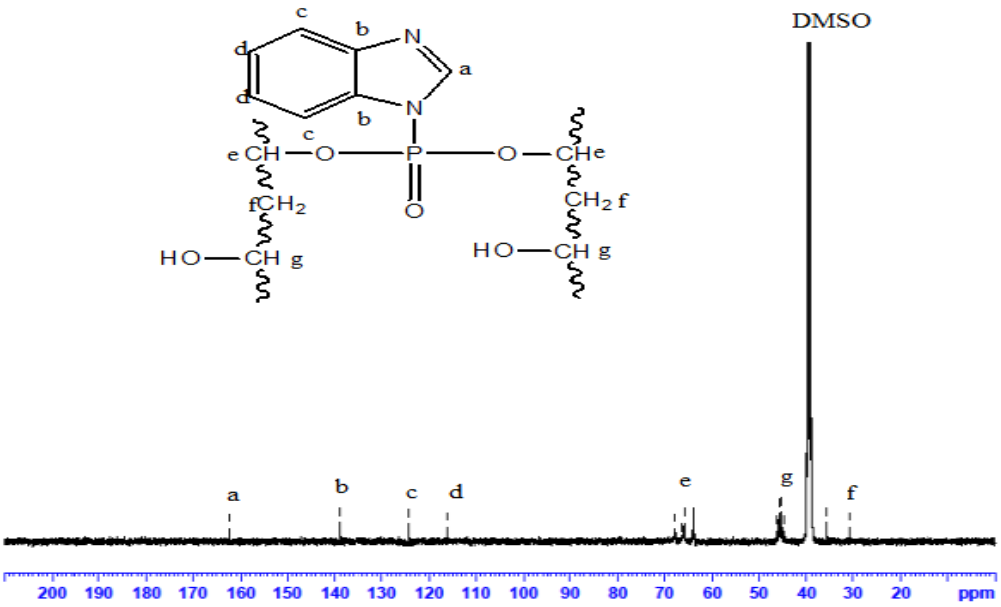

Fig. 2 ^{13}C NMR spectrum of Poly(divinyl benzimidazole-1H-1-yl -phosphonate)

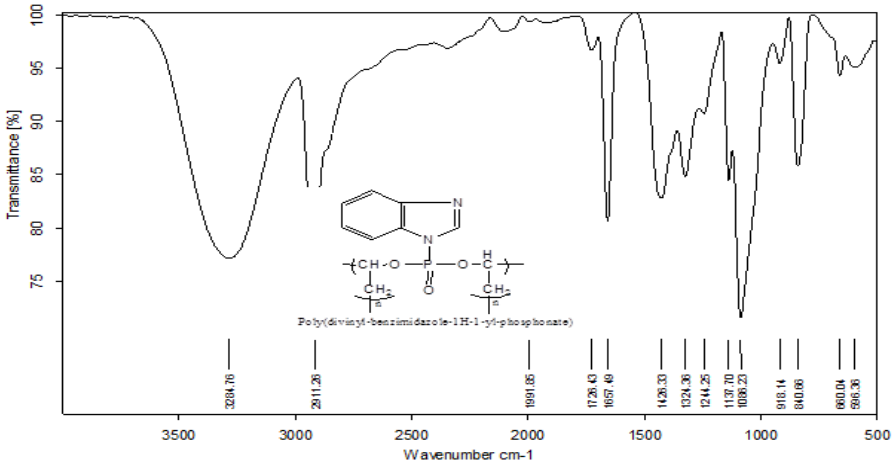

Fig.3 FTIR spectrum of Poly(divinyl benzimidazole-1H-1-yl-phosphonate)

Thermo gravimetric analysis (TGA) is used to get information on thermal stability of the modified polymer. The loss of water also observed for functionalized polymer because of having few percentage of vinyl alcohol (the degree of modification attained only 52-74%). After the initial thermal decomposition, scission of carbon-carbon bonds occurred in heterocyclic modified polymer and reached the maximum decomposition temperature at about 600°C higher than the pure PVA. The 10% char residue at 500°C, 8% char residue at 600°C and Limiting Oxygen Index (LOI) value 21, which are higher the than that pure PVA.

Biological studies of Poly (divinyl benzimidazol-1-yl-1-phosphonate)

The biological activity of the Poly (divinyl benzimidazol-1-yl-1-phosphonate) was tested against a representative number of pathogenic (E.coli, S.aureus, and Bacillus) and results were tabulated.

Table 1: Biological Test report

Biological study	Poly (divinyl benzimidazol-1-yl-1-phosphonate)	ciprofloxacin
Escherichia coli	-	+
Bacillus	+	+
Staphylococcus	+	+

IV. CONCLUSIONS

The N-heterocyclic with phosphorous compound was synthesized and used to modify the hydroxyl functionality of PVA. The formation of the compounds were characterized by FTIR and NMR analysis. TGA Thermograms revealed that modified polymer had excellent thermal stability than the pure PVA. TGA curves were also analyzed to provide an identification of flame retardancy using char yield, which is directly proportional to the LOI.

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