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Synthesis and Characterisation of Polyester Composite Nanofibers for Fungicidal Agents in Textile Industry

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Abstract: In this investigation, we report on the synthesis and characterisation of three new random copolyesters using 4,4'- oxybis(benzoic acid) (OBBA) as common diacid and 1,5-naphthalene diol (ND) as common diol with 4,4'-azodi(benzoic acid) (ADBA)/ 2,6-naphthalene(dicarboxylic acid) (NDCA)/4,4'-biphenyl(dicarboxylic acid) (BPDCA). These polyesters were synthesised by polycondensation method using diphenyl chlorophosphate (DPCP) as condensation agent in pyridine medium. The synthesised copolyesters were characterised by solubility, viscosity measurements, FTIR, ^{1}H and ^{13}C NMR spectral analysis. The composites of the synthesised polyesters were prepared with polyvinylchloride (PVC) and PVC/nanoclay. The nanofibers of the composites were obtained by dissolving the composite in 10% THF using electrospinning method. The morphology of the polyester composite nanofibers was investigated and compared by Scanning Electron Microscopy (SEM) analysis. These composite nanofibers, due to the presence of OBBA and NPDL, are expected to exhibit fungicidal properties and may prove to be valuable candidates for fungicidal textile industry.

Keyword : nanofibers, polycondensation, polymer composites, electrospinning

Introduction

Recent uptrend in the research of polymer composites in the form of nano systems, particularly nano fibers, is astounding. High performance fibers are used increasingly for a wide range of applications including flame retardant, automotive component, thermal insulation, protective clothing and geotextiles for construction[1]. Among these applications, flame retardant fibers are in high demand from the end user[2]. Polyesters synthesized from 4,4'- oxybis(benzoic acid) have been reported to possess intriguing anisotropic, mechanical, electrical and optical properties suitable for technological applications[3]. In general, wholly aromatic thermotropic LCPs received much attention for technological applications due to their ease of processing in the nematic LC phase, high chemical resistance, excellent mechanical and thermal properties. However, they have high melting transition temperature, which limits their use in the processing industry [4]. Polymer nanofibers are potential candidates for a number of applications in medicine, biotechnologically and engineering, because of their large surface area to volume ratio and unique nanometer scale architecture[5]. The polyesters were synthesised by polycondensation using 4,4'-oxybis(benzoic acid) as common diacid and 1,5-

naphtalene diol as common diol with different diacids using diphenyl chlorophosphate (DPCP) as the condensation agent in pyridine medium. In this section we present our work on synthesis and characterisation of copolyesters and studies on the formation of their composite/blend nanofibers.

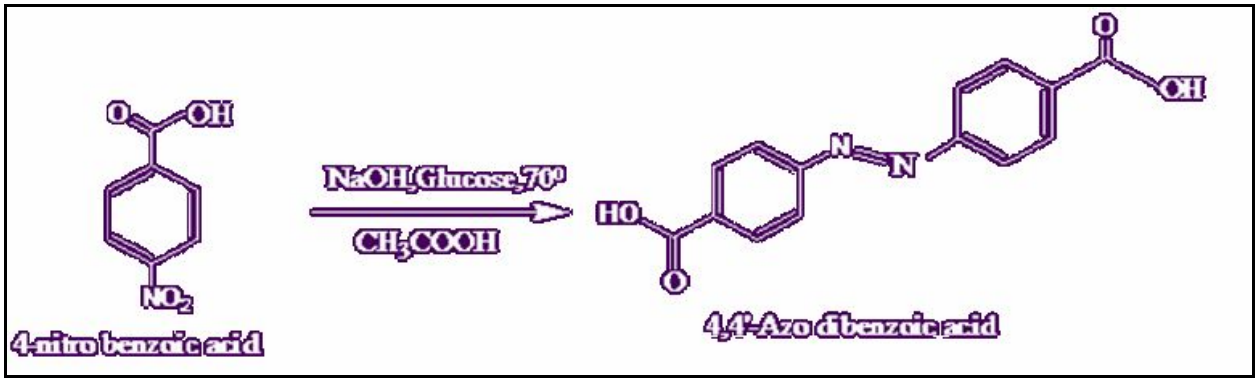
Experimental Methods

Materials:

Pyridine (Merck, 99% pure) was refluxed over potassium hydroxide and distilled (b.p:115^{0}C). 4,4'-azodi(benzoic acid), 4,4'-oxybis(benzoic acid) (OBBA) (99%), 2,6-naphthalene (dicarboxylic acid) (sigma Aldrich),4,4'-biphenyl(dicarboxylic acid) (sigma Aldrich),1,5-naphtalene diol (sigma Aldrich) and diphenylchlorophosphate (DPCP) (99%) purchased from Sigma Aldrich were used as received. Lithium chloride anhydrous (Merck, India) was dried at 130^{0}C under vacuum for 4 h and at 180^{0}C for 10 h. 4-Nitro benzoic acid, dextrose were purchased from SRL. Other solvents such as pyridine, dimethylsulphoxide (Merck), methanol, ethanol, acetone, N, N-dimethyl acetamide (Merck, AR), tetrahydrofuron (Merck), N,N – dimethyl formamide (Mecrk) were distilled before use.

Preparation of monomers:

4, 4'-Azodibenzoic acid used in the synthesis of the polyesters was prepared by the following Tomlinson's method [6-8].



Scheme -1

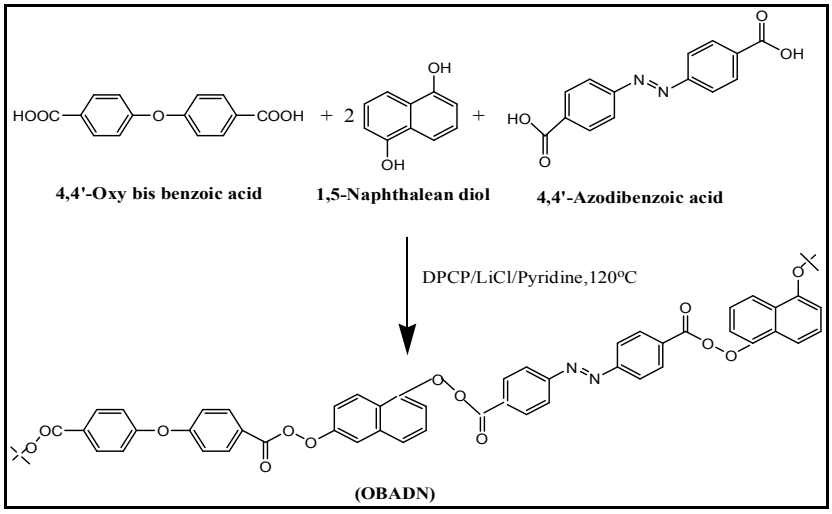
Synthesis of copolyesters:

All the three copolyesters were prepared by direct polycondensation of two diacids and one diol in the respective mole ratio 1:1:2 in pyridine solution using diphenylchlorophosphate (DPCP) as the condensation agent. This method was extensively used by Chang and coworkers[9-10] in the synthesis of several polyesters.

Synthesis of the random copolyesters:

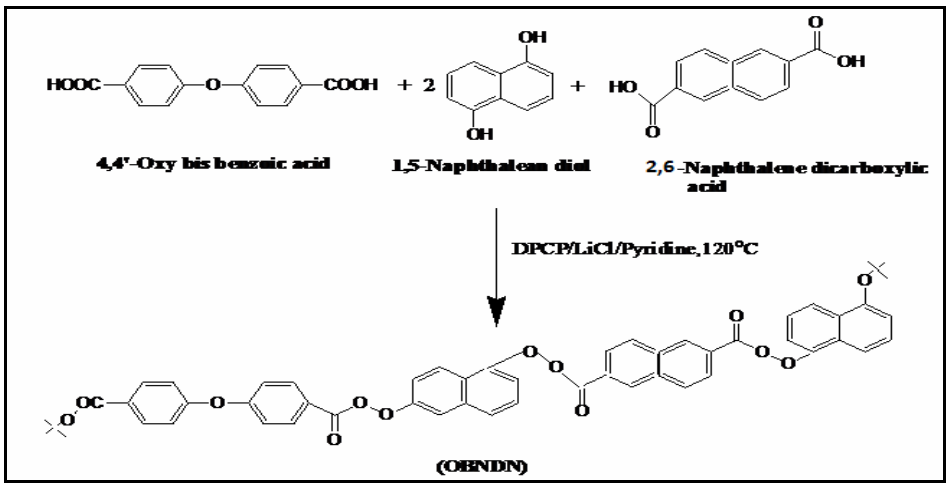
The polymers (Table.1) were prepared by direct polycondensation by the following procedure similar to the one given below. In a three necked 250 mL round bottom flask fitted with a condenser, thermometer and mechanical strirrer in an oil bath, 6.45g of 4,4'-oxybis(benzoicacid), 6.75g of 4,4'-azodi(benzoicacid) in 5 mL pyridine , in 5 mL pyridine and 2.694 mL (13mmol) DPCP were added. After stirring for 20 min, 0.4250g (10mmol) of LiCl in 10 mL pyridine was added and stirring was continued at room temperature for 30 min. The reaction mixture was slowly heated and maintined at 120^{0}C for 20 min. To this mixture, 0.8 g (5mmol) 1,5-naphthalene diol in 10 mL pyridine were added dropwise simultaneously at 120^{0}C for a period of 20 min and the whole solution was further stirred under the same condition for 3hr. The solution was cooled to room temperature and poured into 500 mL water/methanol (1:1 v/v). The product was filtered, washed with hot methanol and dried in vaccum oven at 50^{0}C.

Synthesis of copolyester-I

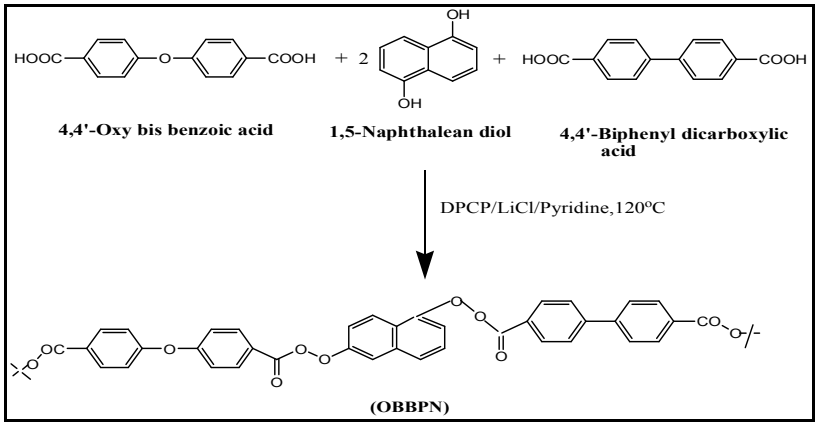


Similarly all of the other polyesters were prepared in the same manner with the same feed ratio.

Synthesis of copolyester-II



Synthesis of copolyester-III



Preparation of polymer blend and nanofiber by electrospinning:

Blending the synthesized copolyesters with PVC was carried out by taking 5 mL of THF in 10 mL closed container and 0.3 g of polyvinyl chloride was added and strirred for 15 min. 0.1 g of polyester was added and strirring continued for 20 min. The solution was removed and placed in an ultrasonicator. The ultrasonicator was run to get homogeneous mixture of sample solution.

A positive voltage was applied to the polymer blend solution through the needle attached to the syringe containing the solution. The solution jet was formed by electrostatic force, when the electrical potential inceased to 22KV. The flow rate of the solution was set at 0.5 mL/h, which was adjusted by computer controlled syringe pump. The distance between the needle tip and collector was maintained at10cm and the drum collector rotation speed around 2350 rpm. The copolyesters/PVC nanofibers in a nonowoven from were collected on an aluminium foil.

Preparation of polymer blend /Layered silicate composite nanofiber formation:

5 mL of THF was taken in 10 mL closed container and 0.3 g of PVC was added and strirred for 15 min then 0.1 gm of polymer, in addition to 10% (w/w) of silicate in the form of nanoclay was added and strirring is continued for 20 min. The solution was removed and placed in an ultrasonicator. The ultrasonicator was run to get homogeneous mixture of sample solution (approximately 10 min). The homogeneous solution was taken in a 2ml syringe and fitted with the adjustable knob of the electrospinning instrument.

Results and Discussion

The copolyesters were synthesized by polycondensation as shown in synthesis of copolyester -I. The polymer codes, monomer codes and yields are listed in Table 1.

Table-1. Yield of the Synthesized Polymers

Polymer Code	Common diacid-I	Varying diacids-II	Common Diol	Yield %
OBADN	4,4'-OBBA	4,4'-ADBA	1,5-NPDL	75
OBNDN	4,4'-OBBA	2,6-NDCA	1,5-NPDL	73
OBBPN	4,4'-OBBA	4,4'-BPDA	1,5-NPDL	70

4,4'-OBBA : 4,4'-oxybis(benzoicacid)
4,4'-ADBA : 4,4'-azodi(benzoic acid)
2,6 –NDCA : 2,6-naphthalene(dicarboxylicacid)
4,4'-BPDA : 4,4'-biphenyl(dicarboxylicacid)
1,5- NPDL : 1,5-naphthalene diol
η_{inh}dL/g : inherent viscosity

3.2. Solubility:

The random copolyesters reported here are found to be soluble in highly polar solvents, partially soluble in moderately polar solvents and insoluble in methanol,hexane. The results of the solubility of polyesters are presented in Table-2.

Table 2. Solubility of copolyesters

Polymer	DMSO	DMF	DMAc	THF	$CHCl_3$	CH_3OH	Hexane	Acetone
OBADN	+-	++	++	++	++	++	++	++
OBNDN	++	--	--	+-	--	--	--	+-
OBBPN	++	++	++	--	--	--	--	+-

Freely Soluble: ++ , Partially soluble: + -, Insoluble: - -

Viscosity measurements:

The inherent viscosity (η_{inh})values of copolyesters were found to be in the range of 0.98-1.13 dL/g as listed in Table-3. It is observed that η_{inh} values of the polymers synthesised using aliphatic diols are lower than that of arylidene diols[11].

Table -3:Inherent viscosity (η_{inh}) values

S.No	Polymer Code	η_{inh}dL/g
1	OBADN	1.05
2	OBNDN	0.98
3	OBBPN	1.13

Spectral Characterization

All the three co-polyesters synthesised from 4,4'-oxybis(benzoic acid) are more soluble. The inherent viscosity of the co-polyesters was determined in N, N-dimethylacetamide (DMAc) solution at 30^{o}C using an Ubbelode viscometer. The solubility of these polyesters ws tested in various solvents qualitatively. IR spectra of the co-polyesters were recorded using Nicolet 510 FT-IR analyser with their neat films in KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded with PROPHD and PULPROG -500 MHz instrument in DMSO-d_6 solvent with TMS as internal reference. The morphology of the polymer blend nanofibers were derived from Espin-Nano electrospinning machine, PECO, Chennai-India. The SEM photomicrographs of the polyesters were recorded with Hitachi S-3400 SEM instrument.

FT-IR Spectral analysis:

The FT-IR spectra of the random copolyesters OBADN, OBNDN and OBBPN were recorded and presented in Fig.1-3. All the three FT-IR spectra possessed a split absorption characteristic for the two types of carbonyl groups present in the polyesters. The peaks at 1735-1788 cm^{-1} indicate C=O stretching vibrations of the aromatic ester group. The absorptions due to C-O stretching are also observed in the range 1242-1249 cm^{-1} for all the copolyesters. It is inferred that the monomers are incorporated into the polyesters backbone.

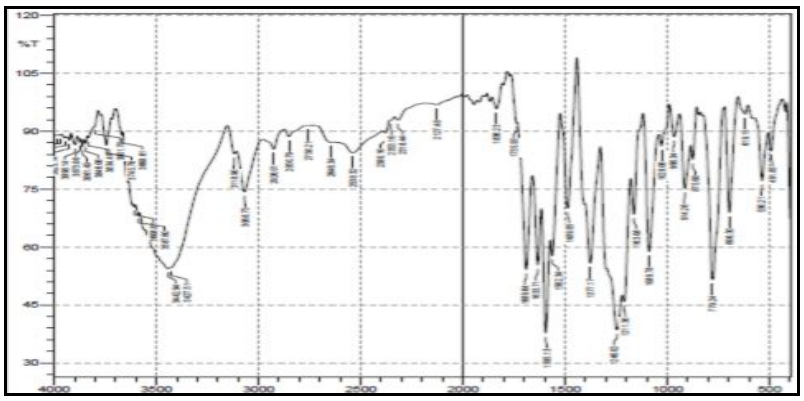


Figure.1: FTIR spectrum of OBADN Polyester

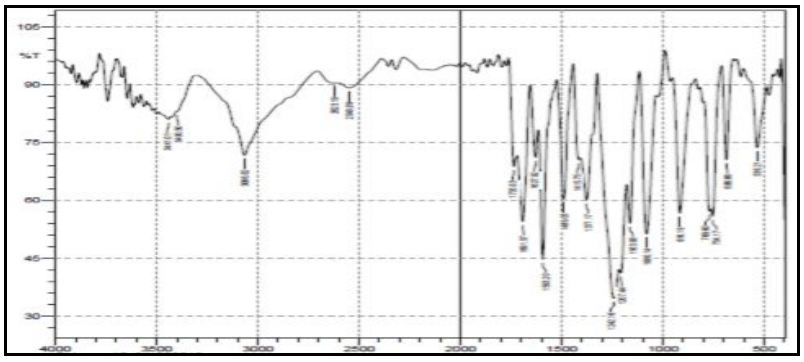


Figure.2: FTIR spectrum of OBNDN Polyester

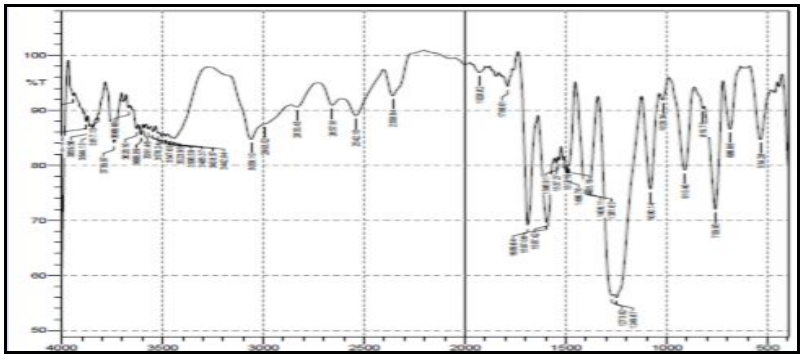


Figure.3: FTIR spectrum of OBBPN Polyester

^{1}H NMR-Spectra:

The repeating units in the polymer chain were identified by NMR spectral analysis. The ^{1}H NMR of the synthesized polymers were recorded in using DMSO-d_6 as solvent and presented in figure 4. The chemical shift values observed in the range of 7 to 8.01 shows the aromatic protons of the synthesised polymers.

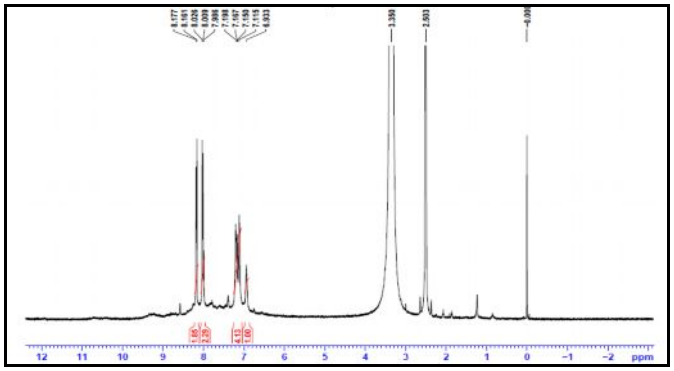


Fig-4: ^{1}H NMR spectrum of polyester OBADN

Morphological study by SEM:

The electrospinning process was successfully used to embed copolymer OBBPN in a polyvinylchloride (PVC) matrix, forming blend nanofibers. The polymer blend fibers were characterized by FT-IR, ^{1}H, ^{13}C and SEM images, the average diameter of this composite nonfibers was found to be 176-431 nm. The nonofibersof other polymers were found to be smooth surface and uniform in morphology.

Usually aromatic polyesters have rigid structure because of this feature these have very low solubility in most organic solvents. This is a handicap which affects the formation of polymer solution and hence processability of the polymer. Alternatively solubility problem is averted by blending them with other polymers like PVC, PVA etc., PVC is a multifunctional polymer which is widely used in the world for various applications.

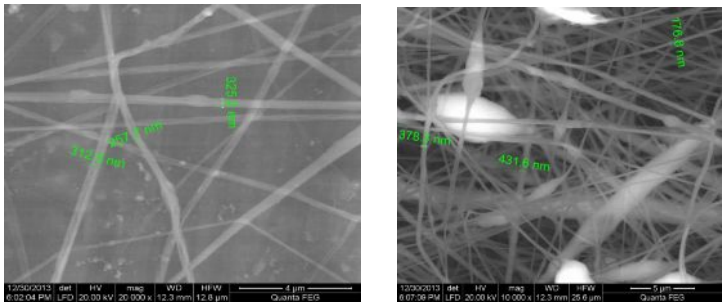
The electrospinning process was successfully used to embed copolymer OBBPN in a polyvinylchloride (PVC) matrix, forming composite nanofibers. The polymer blend fibers were characterized by SEM Images. The attempts to prepare nano fiber of OBBPN in THF and various other organic solvents by electrospinning were unsuccessful. The SEM image of OBBPN without blending shows the formation of nano structured grains (Fig-5) but the fiber formation is very low or negligible. After several attempts to form neat composite fiber by various blending compositions, it was observed that OBBPN/PVC blend (ratio 1:3) produced neat fiber on electrospinning.

OBBPN/PVC nanofibers

The fibers are uniform, well dispersed and without knot on their surface. The surface of the fibers have slightly rough surface while PVC shows smooth surface, the change on the surface occurs only due to the blending of OBBPNwith PVC. From SEM images, the average diameter of these OBBPN/PVC blend nanofibers was found to be 300-900 nm. All images show the fiber formation clearly with controlled size and shape. There is no significant disruption in the fiber structure due to the addition of OBBPN to PVC. This composite fiber of OBBPN/PVC blend was found to possess enhanced strength than the pure PVC fiber. The SEM image of OBBPN in PVC matrix were shown in Fig-5.

Polymer / PVC / Layered silicate composite Nanofiber formation:

5 ml THF was taken in 10 mL closed container with pellet in which 0.3g of polyvinylchloride was added and stirred for 15 min and then 0.1 g of OBBPN, in addition to10% (w/w) of silicate in the form of nanoclay was added and stirring continued for 20 min. The solution was removed and placed in an ultrasonicator. The ultrasonicator was run to get homogenous mixture of sample solution (approximately 10 min). The SEM image of OBBPN/PVC/ Layered silicate composite Nanofiber.



a) **b)**

Fig-5: SEM images of Polymer a) OBBPN/PVC b) OBBPN/PVC/ Nanoclay composities

Conclusion

A series of three new copolyesters were synthesized by direct polycondensation using diphenyl chlorophosphate and lithium chloride in pyridine. The common dicarboxylic acid used is 4,4'-oxybis (benzoic acid) and different diacids 2,6-naphthalene dicarboxylic acid and 4,4'-biphenyl dicarboxylic acid with the common diol 1,5-naphthalene diol. The inherent viscosity data reveal that the synthesised copolyesters are high molecular weight materials. These copolyesters were characterized by viscosity measurements, FT-IR, ^{1}H-NMR, and ^{13}C-NMR. Blending of the copolyesters derived from 4,4'- dicarboxlic acid with PVC/nanoclay produced neat fibers with diameter in the nano range. The SEM images of copolyester blend fibers show excellent fibrous structure at the nano level which may be utilized for fungicidal applications as reported earlier due to the presence of 4,4'-oxybis(benzoic acid)[12].

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