Synthesis and Characterization of Certain Copolyester-PVC-Nanoclay Composites Possessing Arylidene-Cyclohexanone Moiety in the Main Chain

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Abstract— **A series of three random copolyesters were prepared from a dicarboxylic acid, a diol – I and a diol – II in the mole ratio of 2:1:1 by direct polycondensation with diphenylchlorophosphate (DPCP) as the condensation agent. The diacid used is 2,6-napthalenedicarboxylic acid. The diol–I also referred as a common diol namely 2,5-bis(4-hydroxy 3-methoxy benzylidene)cyclohexanone was prepared by acid catalyzed Claisen-Schmidt reaction. The diol – II a variable diol used are 1,8-dihydroxyanthraquinone, 1,5-dihydroxynaphthalene and phenolphthalein. These copolyesters were characterized by qualitative solubility tests, viscosity measurements and their microstructure in the copolyester main chain is determined by FT-IR, ^{1}H and ^{13}C NMR spectroscopic studies. The phase transition temperatures of these copolyesters were investigated by DSC thermograms. Copolyester-nanocomposites were prepared with polyvinylchloride (PVC) and nanoclay in tetrahydrofuran medium in 10% (w/w) ratio and the nanofibers were obtained by electrospinning method. The morphology of these copolyester composite nanofibers was investigated by scanning electron microscopy (SEM). These nanofibers may emerge as potential flame retardant materials besides being used for medical drug delivery systems.**

Keywords- **arylidenecyclohexanone, polycondensation, copolyesters-nanocomposites, nanofibers**

I. Introduction

An exhaustive survey of literature conspicuously unveil that arylidene-cyclohexanone-based polymeric composite fibers facilitated drug delivery. Arumugasamy [1] has synthesized a number of random copolyesters containing 4,4´-dihydroxybis(arylidene)cycloalkanones using aliphatic diacid chlorides and found that they exhibited thermotropic liquid crystalline (TLC) behaviour. Kannappan *et al* [2]. investigated the rate of photocrosslinking of the random copolyesters with arylideneketo moiety by UV spectral studies. Even poly(ester-amides) were synthesized by making use of arylidene-ketones [3]. However, literature survey indicates that there are few reports on the synthesis and characterization of certain multifunctional copolyester-PVC-nanoclay composites possessing arylidene-cyclohexanone moiety in the main chain of the copolyster. Hence, we were interested to synthesise and characterize certain copolyester-PVC-nanoclay composites possessing arylidene-cyclohexanone moiety in the polymer.

II. Experimental detail

Aldrich samples of vanillin, cyclohexanone, 2,6-napthalenedicarboxlic acid, 1,8-dihydroxy anthraquinone, 1,5-dihydroxy naphthalene, phenolphthalein and Merck samples of tetrahydrofuran (THF), DMSO-d6 and sulphuric acid were used as received. Methanol (Merck) was used as a non-solvent for the precipitation of copolyesters and as a solvent for the preparation of the monomer diols. SD Fine AR sample of dimethyl acetamide (DMAc) was used as such as solvent for finding out the inherent viscosity of the copolyester in solution. NMR Spectra. was used as solvent in the preparation of the copolyester composites.

The arylidene diol namely 2,5-bis(4-hydroxy 3-methoxy benzylidene)cyclohexanone was prepared by the method reported by Sidharthan and coworkers [5] given in the following scheme.

4-hydroxy3-methoxy benzaldehyde → 2,5 bis[(4-hydroxy 3-methoxy (benzylidene)] cyclohexanone
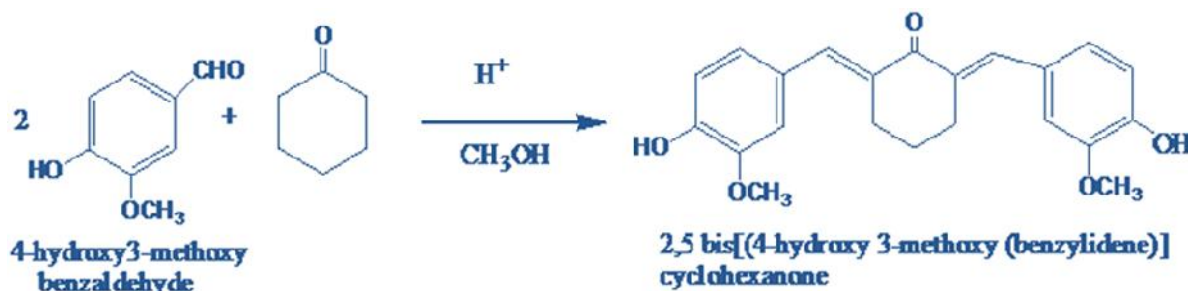
A. Synthesis of Copolyester

The three copolyesters namely PNBA, PNBN and PNBP were prepared by the method reported by Arulmoli and coworkers [5]. Table 1 gives the monomers used in the synthesis, their codes, yield percentage and inherent viscosity.

Table-1

Common Diol: 2,5-bis(4-hydroxy 3-methoxy benzylidene)cyclohexanone		**Copolyester Code**	**Yield (%)**	inh (dL/g)
Diacid	**Diol-II**			
2,6-napthalenedicarboxlic acid	1,8-dihydroxy anthraquninone	PNBA	74.5	0.971
2,6-napthalenedicarboxlic acid	1,5-dihydroxy naphthalene	PNBN	76.2	0.934
2,6-napthalenedicarboxlic acid	Phenolphthalein	PNBP	71.7	0.927

B. Synthesis of Copolyester-PVC-Nanoclay Composites by Elecrospinning Method

This method was reported by Mayavathi *et al* [6].

C. Preparation of Blend Solution

About 0.6 g of polyvinylchloride, 0.2 g of PNBA and 5mL of THF were taken in a 10mL closed container and stirred well for about 2 hours. Then it is taken in an ultrasonicator bath for an hour to ensure that the copolyester and the PVC were well dispersed in THF medium. As a last step stirring for 24 hours was carried out by using a magnetic stirrer.

Similar procedure was adopted to generate the copolyester-PVC-nanoclay composite by taking the PVC, the copolyester and the nanoclay in the ratio of 1:3:1.

D. Blend Fibers Preparation

The homogeneous solution was taken in a 2 mL syringe and positive voltage was applied to the blended solution through the needle attached to the syringe. The solution jet was formed by electrostatic force, when the electrical potential was increased to 22 kV. The flow rate of the solution was set at 0.4 mL/h, which was adjusted by means of a computer controlled syringe pump. The distance between the needle tip and the collector was maintained at a distance of 10 cm and the drum collector rotation speed of about 1800 rpm. The PNBA/PVC nanofibers in a nonwoven form were collected on an aluminum foil.

III. Results and Discussion

Solubility of all the copolyesters was determined in various solvents qualitatively. The inherent viscosity (inh) of the polyesters was determined in DMAc solution using Ubbelohde viscometer at 30°C. FT-IR spectra of the entire random copolyesters were recorded using Shimadzu FT-IR instrument. The ^{1}H and ^{13}C-NMR spectra were recorded with BRUKER AV III 500 MHz NMR instrument in DMSO-d6 solvent. DSC thermograms of all the three copolyesters were obtained using DSC 200 F3 MAIA instrument. The SEM photomicrographs of the Copolyester -PVC and Copolesters-PVC/Nanoclay Composites were recorded with Hitachi   S-4800 SEM instrument.

A. Solubility

The three copolyesters reported here are found to be soluble in highly polar solvents such as DMAc and dimethyl formamide, partially soluble in moderately polar solvent like acetone but thoroughly insoluble in least polar solvents like benzene and n-hexane.

B. Viscosity Measurements

The   inh value of all the three copolyesters was determined in DMAc solution at 30°C using Ubbelohde viscometer. In each case 25mg of pure dry copolyester sample was dissolved in 25ml of DMAc, kept aside for some time with occasional shaking. The inherent viscosity values were found to be in the range of 0.927–

0.971dL/g and are presented in table 1. The data shows that these copolyesters are reasonably of high molecular weight.

C. Spectral Studies

FT-IR spectrum of the three copolyesters was recorded using Shimadzu FT-IR instrument. The FT-IR spectrum of all the three copolyesters showed characteristic absorption in the range of 1732–1738cm^{-1} due to ester C=O stretching frequency. Similar observations were made by Arul Moli and coworkers [8] in a series of copolyesters. A typical FT-IR spectrum of the copolyester PNBN is given in figure 1.
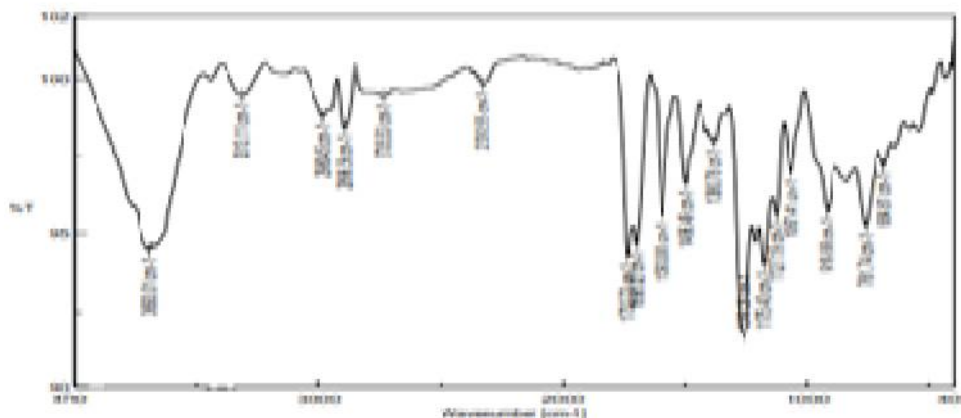

Figure 1: FT-IR Specrum of the Copolyester PNBN

The NMR spectra were recorded with BRUKER AV III 500 MHz NMR instrument in DMSO-d6 solvent to identify the structural units present in the copolyester chain. The aromatic protons are observed in the range of 7.1–8.5ppm. The vinyllic protons attached to the carbonyl carbon are observed in the range of 6.8–7.0ppm. The methylene protons of the cyclohexanone ring are observed in the range of 2.0–3.0ppm. Similar remarks were made Kannappan and coworkers [3] in a series of copolyesters derived from arylidene diols. A typical H^{1}-NMR spectrum of the copolyester PNBN is given in figure 2.
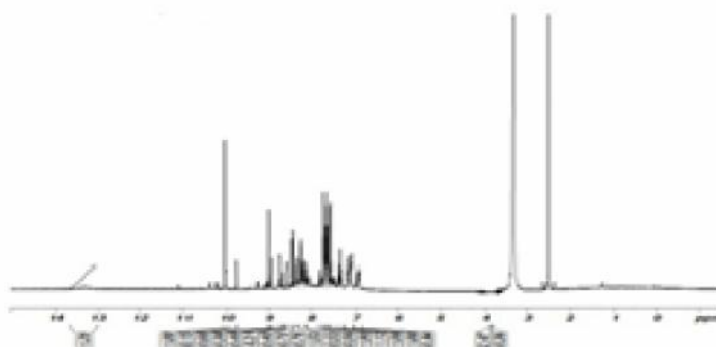

Figure 2: H1-NMR Spectrum of the Copolyester PNBN

The signals in the range of 190-195ppm and 150-165ppm in the 13C-NMR spectra of the copolyesters are owing to the carbonyl carbon of the ester groups, respectively, which indicates the formation of copolyester.

D. Thermal Characterization

Differential scanning calorimetry was employed to obtain DSC thermograms for the copolyesters PNBN, PNBA and PNBP. Their phase transition temperatures in the first scan with the heating rate of 10°C/min

are summarized in Table 2. From table 2 it is clear that all the three copolyesters have the T_g values higher than 140°C which is due to the presence of wholly aromatic moieties in the copolyester backbone. But the presence of flexible spacers will reduce the T_g values lesser than 70°C. This was observed by Sidharthan and coworkers [4] in a series of copolyesters.
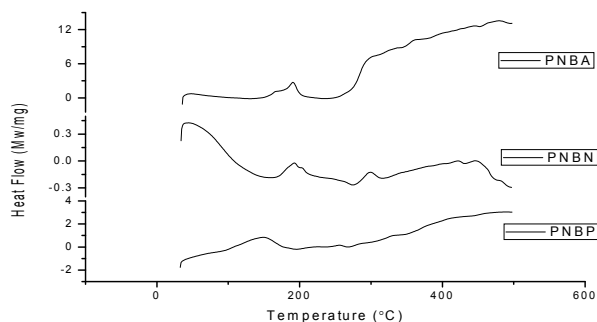

Figure 3: DSC Thermograms of the Copolyester PNBN, PNBA and PNBP

Copolyester Code	T_g (°C)	T_m (°C)	T_{cl} (°C)
PNBA	190	298	360
PNBN	192	297	447
PNBP	148	255	329

E. SEM Studies

Scanning electron microscopy (SEM) is applied to picture the topography of the polymeric material [9,10]. The electrospinning method was effectively utilized to embed copolyester in a polyvinylchloride (PVC) matrix, forming blend nanofibers. The polymer blend fibers were characterized by SEM Images. The SEM micrographs of the PVC-PNBA Composite, the PVC-PNBA-Nanoclay Composite, the PVC-PNBN Composite, the PVC-PNBN-Nanoclay Composite, the PVC-PNBP Composite and that of the PVC-PNBP-nanoclay Composite are represented in figures 4.
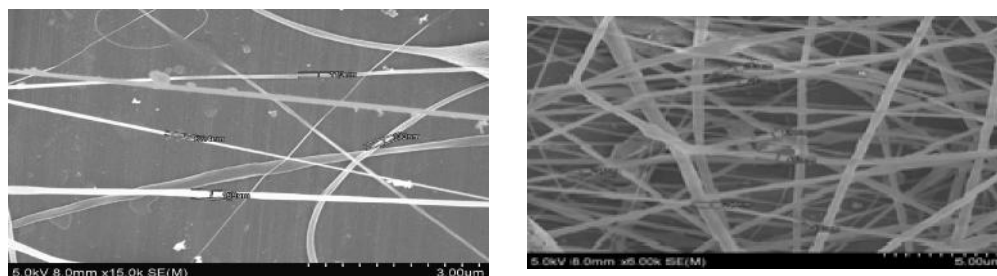

Figure4: SEM images of (a) PNBA/PVC (b) PNBA/PVC/ Nano Clay Composites

The SEM images of the representative copolyesters in PVC matrix indicates that the copolyester/PVC fibers spun by electro spinning method exhibited spherical diameters and smooth surfaces in a uniform fashion. The SEM micrographs display that the fibers are uniform f with diameter range of 67-450 nm and are well dispersed

without beads on their surface. There is no significant disruption in the fiber structure due to the addition of polyester to PVC. Parallel observations were made by Mayavathi *et al* [6] in a series of certain random copolyester/PVC composites.

IV. CONCLUSION

A series of three new copolyesters were synthesized by direct polycondensation using diphenylchlorophosphate and lithium chloride in pyridine. The dicarboxylic acid used is 2,6-naphthalene dicarboxylic acid and the common diol used is 2,5-bis(4-hydroxy 3-methoxy benzylidene)cyclohexanone. The variable diols used are 1,8-dihydroxy anthraquinone, 1,5-dihydroxy naphthalene and phenolphthalein. The inherent viscosity data reveals that the polymers are high molecular weight materials. The synthesized copolyesters were characterized by viscosity measurements, FT-IR, ^{1}H-NMR, and ^{13}C-NMR. Thermal transition temperatures of copolyesters were determined from DSC thermograms. Nanofibers of the copolyester could be conveniently fabricated by electrospinning with spinnable PVC matrix polymer solution. Blending of the copolyesters derived from 2,6-napthalenedicarboxlic acid with PVC produced neat fibers with diameter range of 67-450 nm. The SEM images of copolyester blend fibers show excellent fibrous structure at the nano level which may be utilized for flame retardant applications because of their high thermal stability. Reports also indicate that these polymeric composite materials could be used for drug delivery.

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