Morphology and miscibility of chitin–polyaniline blend

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In this article, we discuss the blending of chitin with polyaniline (PANI) and its miscibility. Miscibility of the chitin–PANI blend has been studied by solution viscometry, Fourier transform infrared (FTIR) spectrum and scanning electron microscope (SEM) techniques. From viscosity measurement Krigbaum and Wall polymer–polymer interaction parameter (Δb) is calculated; it is found to be positive for all compositions of the blend. From FTIR analysis, probable interaction is predicted. Viscosity measurement of chitin and PANI blends shows a linear relationship between intrinsic viscosity and blend composition with a positive deviation from the theoretical value and positive value of Δb refers to the miscibility of the blend system. From SEM studies, blends having 5% lithium chloride (LiCl) show a homogeneous and continuous structure. Blends having less than 5% LiCl show a homogeneous and fibrillar structure, which is further supported by atomic force microscopy studies. Fibrous structure improves as the amount of PANI increases. FTIR analysis confirms the interaction between chitin and PANI. Further, this result is supported by DSC, TGA, XRD and dissolution studies of the blend.

**Keywords:** Biopolymer, blending, chitin, miscibility, polyaniline.

POLYANILINE (PANI), a conducting polymer, has attracted considerable attention recently because of wide spectrum of applications such as electromagnet interference shield, gas sensor, biosensor, battery, polymeric light emitting diode, etc. due to the combination of unique properties like good environmental stability, relatively high conductivity, simple preparation, simple doping procedure and low cost[1,2]. However, its poor mechanical properties and processibility due to its insoluble nature in common organic solvents are major problems in successful utilization[1–6]. In order to overcome this problem, PANI is blended with other insulating polymers.

Chitin is a natural polysaccharide composed mainly of β-(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose and partially of β-(1,4)-linked-2-deoxy-2-amino-D-glucopyranose[7–10] (Figure 1). After cellulose, chitin is the second most abundant natural polymer, commonly found in exoskeletons or cuticles of many invertebrates and in the cell walls of most fungi and some algae. It is normally obtained from the shells of shrimp, crab, lobster or shellfish. Several important advantages such as biodegradability, biocompatibility, high mechanical strength and nontoxicity of chitin have attracted attention[7,9].

Depending on the oxidation level, PANI exists in different forms and can be synthesized in various insulating forms such as fully oxidized pernigraniline base, half oxidized emeraldine base (EB) and fully reduced leucoemeraldine base. Among these three forms, EB (Figure 2 a) can be made conducting and its conductivity varies from 10^{-10} S/cm to 10^2 S/cm on doping; the other two forms cannot be made conducting. Protonic acid-doping of EB will lead to the formation of conducting emeraldine salt form (Figure 2 b)[1,2,10,11].

Properties of conducting polymers can be modified using an important technique called polymer blending. Properties of conducting polymers are governed by a molecular-level miscibility between component polymers. Physical properties of immiscible polymer blends are poor compared with those of parent polymers due to phase separation arising at the boundaries of component polymers. Intermolecular interaction such as dipole–dipole interaction and hydrogen bonding between component polymers will improve the miscibility and physical properties of blends. Several studies have been reported in recent years on blending or grafting of PANI with chitin and its derivatives[12–15]. The miscibility of PANI blend by viscometric studies and also the effect of lithium chloride (LiCl) on the morphology of the blend has been reported[2]. Possible interaction mechanism is also explained from the Fourier transform infrared (FTIR) analysis.
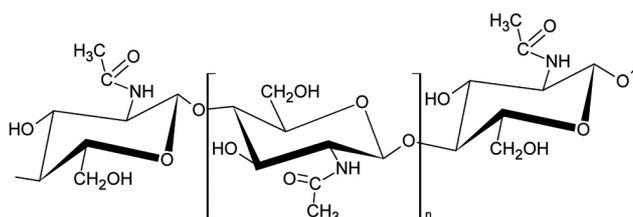
Figure 1. Structure of chitin.
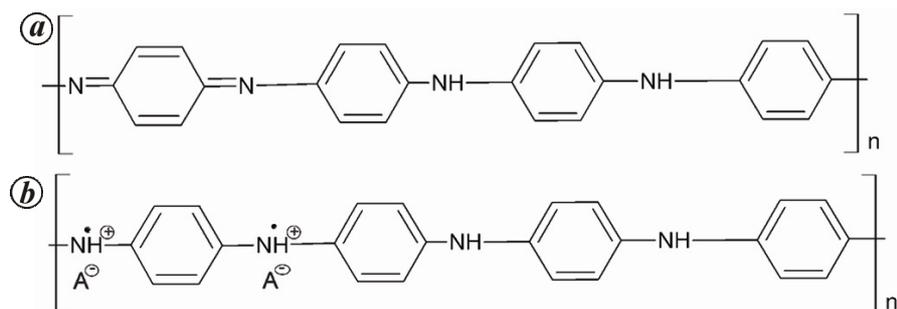
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Figure 2. Structure of (*a*) polyaniline emeraldine base and (*b*) polyaniline emeraldine salt.

Chemicals and materials used

Freshly distilled aniline under reduced pressure and ammonium peroxy disulphate (APS), both GR-grade, were obtained from MERCK, India. Chitin (molecular weight 400,000 g/mol) was supplied by HIMEDIA, Mumbai *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMA), *N*-methyl pyrrolidine (NMP) and LiCl, all AR-grade, were obtained from SRL. All chemicals were used as received.

Experimental procedure

Preparation of polyaniline

PANI was prepared as reported by MacDiramid and Epstenin *et al.*[16]. Required amount of aniline was dissolved in 1 M HCl to get 0.25 M aniline solution, which was cooled to 0°–5°C. Pre-cooled 0.25 M APS solution prepared in 1 M HCl was added dropwise in 20 min interval. The reaction mixture was stirred for 1 h by maintaining temperature at 0°–5°C and then stirred for three more hours without maintaining temperature. The resultant green precipitate of PANI was filtered and washed with 1 M HCl, deionized water and finally with acetone respectively and then dried for 24 h at 60°C. Green flakes of PANI were powdered and treated with 0.5 N NaOH solution for 16 h to get EB, which was washed with water until it became neutral. Viscosity average molecular weight of the polymer was found to be 1.03×10^5 g/mol.

Blend preparation

Blends of chitin and polyaniline were prepared using the common solvent technique. DMA is a solvent for chitin in the presence of 5% LiCl and non-solvent in the absence of LiCl. PANI is soluble in DMA in the presence of 5% LiCl as well as in the absence of LiCl. Blends of chitin with PANI 30%, 50% and 70% (P30, P50 and P70) were prepared by mixing 0.5% chitin solution in DMA with 5% LiCl and 0.5% EB solution in DMA with 5% LiCl (in order to maintain ionic strength of LiCl as 5%) in required proportions. We also prepared the blend by

mixing 0.5% chitin solution in DMA with 5% LiCl and 0.5% EB solution in DMA without LiCl (without maintaining ionic strength of LiCl) in required proportions. Hence in the second case effective percentage of LiCl varied according to the proportion of chitin solution in the blend, i.e. LiCl percentage in P30 was 3.75%, P50 2.5% and P70 was 1.25%. The same blend solutions were used for viscosity measurements. Blend films were prepared by solution casting on glass petri dishes and drying at 70°C. The films thus obtained were washed with water, then with acetone and dried at 60°C for 24 h. The thickness of the films was approximately 40 μm.

Physical characterization

Viscosity measurements for pure and binary systems were carried out at 30°C using Ubbelohde U-tube viscometer immersed in a constant temperature bath with a temperature accuracy of ±0.1°C. Perkin-Elmer FTIR spectrophotometer (model 1000) was used for recording FTIR spectra of the blends. Scanning electron microscope photomicrographs of the surface of blend films coated with gold were taken using SEM (model: JEOL JSM 5800CV). AFM images were recorded using atomic force microscopy (AFM) machine. Differential scanning calorimetry (DSC) analysis was carried out using SHIMODZ DSC-50. Thermogravimetric analysis (TGA) was carried out using Perkin Elmer, Diamond TG/DTA machine, in nitrogen atmosphere, from room temperature (25°C) to 600°C at a heating rate of 10°C/min.

Theory

The interaction and miscibility in solutions of polymers blends can be evaluated using simple viscometry method. Solution-state miscibility evaluated by the viscosity method can be correlated to bulk solid-state miscibility of polymer blends[17,18]. From viscometric technique, Krigbaum interaction parameter term (Δb) can be obtained; Δb is positive for miscible blends and negative for immiscible polymer blends[17–22]. Thus using viscometric technique we can predict the solid-state miscibility of polymer blends.

The specific viscosity $(\eta_{sp})_m$ for polymer blend solution can be expressed as[19]

$$\frac{(\eta_{sp})_m}{C_m} = [\eta]_m + b_m C_m, \qquad (1)$$

where $C_m = C_1 + C_2$ is the total concentration of polymers. $[\eta]_m$ is the intrinsic viscosity of the blend which is defined as

$$[\eta]_m = [\eta]_1 C_1 + [\eta]_2 C_2, \qquad (2)$$

and b_m is the global interaction between all polymeric species and is defined as

$$b_m = C_1^2 b_{11} + 2C_1 C_2 b_{12} + C_2^2 b_{22}, \qquad (3)$$

where b_{11} and b_{22} are specific interaction coefficients of component polymers 1 and 2 respectively, and b_{12} is the specific interaction coefficient for the polymer blend of component polymers 1 and 2.

The coefficient b_{11} is related to the constant k_1 in the Huggins equation (eq. (4)), for polymer 1. This applies to b_{22} also

$$\frac{\eta_{sp}}{C} = [\eta_1] + k_1 [\eta_1]^2 C. \qquad (4)$$

The relationship between b_{11} and k_1 can be written as

$$b_{11} = k_1 [\eta_1]^2, \qquad (5)$$

where k_1 is the Huggins constant for component polymer 1 in solution. From eqs (1), (3)–(5) we can determine the experimental value of b_{12}. The theoretical interaction coefficient b_{12}* between two polymers can be expressed as

$$b_{12}^* = (b_{11} b_{22})^{1/2}. \qquad (6)$$

As described by Krigbaum and Wall[19], information on the intermolecular interaction in binary polymer blends can be obtained from a comparison of experimental and theoretical values of interaction coefficients. Hence miscibility of binary blends can be simply characterized by the interaction parameter term Δb

$$\Delta b = b_{12} - b_{12}^*. \qquad (7)$$

$\Delta b > 0$ signifies miscibility and $\Delta b < 0$ indicates phase separation. If η_1 and η_2 values are sufficiently apart, a more effective parameter μ can be used to predict the compatibility

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2}. \qquad (8)$$

A positive value of μ indicates miscibility.

Results and discussion

The miscibility of chitin–PANI blend system was evaluated from the viscosity measurements in solvent DMA with 5% LiCl. From viscosity measurements, reduced viscosities of parental polymer and their blends were found. Reduced viscosity versus concentration was plotted for component polymers and their blend compositions (P30, P50 and P70; Figure 3). In these plots, no crossover is seen and they are linear, which means the blends are compatible. In the case of incompatible blends, a sharp crossover is observed[23]; intrinsic viscosity values of individual polymers and their blend compositions are obtained from the intercept of reduced viscosity versus concentration plots. The obtained experimental intrinsic viscosity values were compared with theoretical values predicted from weighed averages (Table 1). The experimental intrinsic viscosity value was slightly higher than the theoretical values (Figure 4). That is due to the interaction between the polymer chains. The intrinsic viscosity always shows a negative deviation for immiscible systems, due to the repulsive interaction between polymers[17]. The interaction parameter b of the parental polymers and their blend compositions was found from the plots of the reduced viscosity versus concentration. The slope of the curve gave the corresponding b values (Table 1). Krigbaum and Wall interaction parameter Δb was calculated using eqs (1)–(7), while μ was calculated using eq. (8). It was found that both Δb and μ were positive (Table 1), which clearly indicated that blends of chitin and PANI were miscible for all the studied compositions. Also Δb value was high for the compositions P50 and P70.

Figure 5 shows the FTIR spectra of PANI, chitin and their blends. IR spectra of blends show significant peaks of both chitin and PANI. The characteristic peaks of PANI are observed at ≈835, ≈1153, ≈1259, ≈1431 and
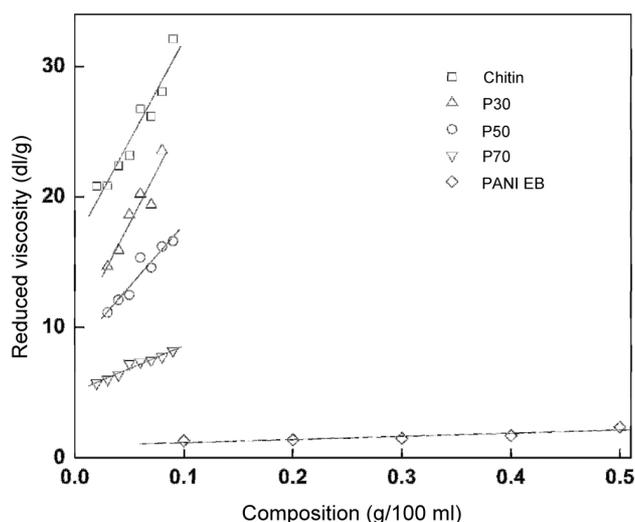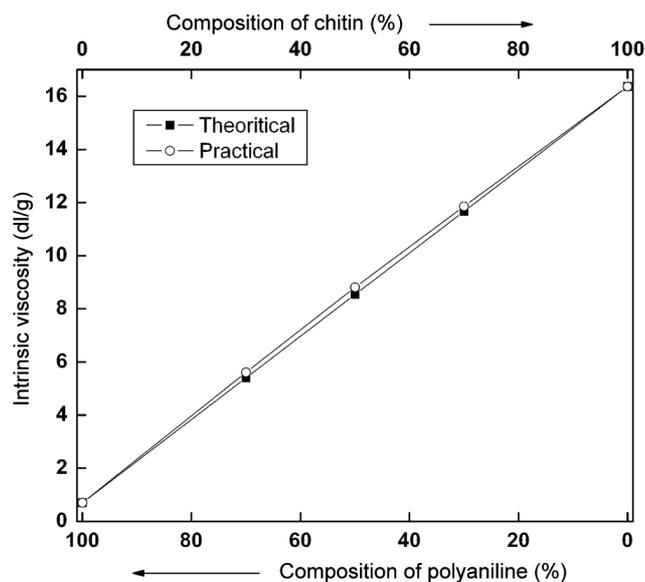

Figure 3. Reduced viscosity versus concentration curve.

Table 1. Intrinsic viscosity and interaction parameters of polyaniline (PANI) and chitin (CHI) blends

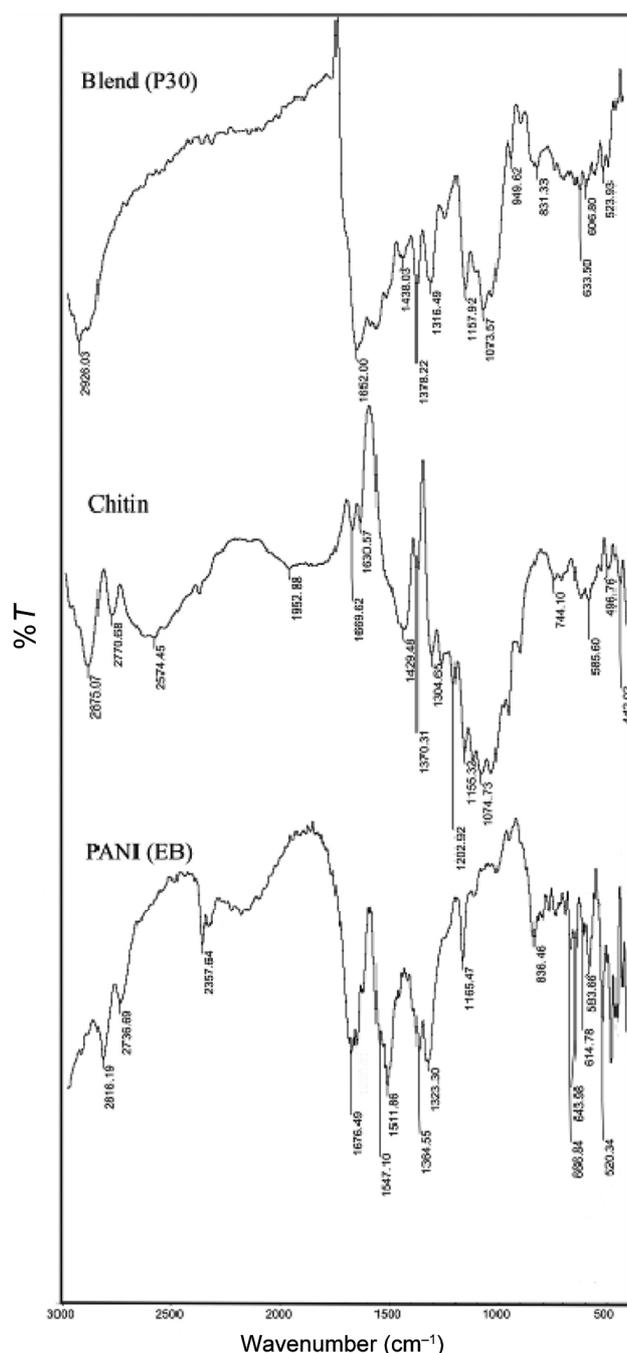| Blend composition PANI/CHI	Intrinsic viscosity		Slope of red viscosity versus concentration plot	Experimental b_{12} value	Theoretical b_{12}*	Δb	μ
	Experimental (dl/g)	Theoretical (dl/g)					
100/0	0.7	0.7	2.46	–	–	–	–
70/30	5.61	5.4	24.84	59.54	19.77	39.77	0.162
50/50	8.81	8.54	71.45	62.24	19.77	42.47	0.173
30/70	11.86	11.67	103.07	22.23	19.77	2.46	0.01
0/100	16.37	16.37	158.86	–	–	–	–

Figure 4. Intrinsic viscosity versus concentration curve.

≈1519 cm^{-1} (refs 24–27) and also significant peaks of chitin are observed in the blend. The band at ≈1519 cm^{-1} is attributed to benzenoid and quinoid unit stretching modes of PANI and the band at ≈1153 cm^{-1} is attributed to quinoid unit of doped PANI[24]. The IR spectrum of chitin (Figure 5) shows peaks of hydroxyl group and carbonyl group at ≈3256 and ≈1669 cm^{-1} respectively[8,11]. However, the carbonyl group peak shifted to ≈1650 cm^{-1} in the blend. This is due to the interaction between PANI and chitin. The interaction was further verified from the dissolution studies in DMF, NMP and DMA. Even after a week only a negligible portion of PANI was obtained from the blend in these solvents (Figure 6).

Systems containing amide groups can interact with LiCl, giving rise to physically cross-linked polymers, due to an ion–dipole interaction between the principal donor site oxygen in the amide and the Li$^+$ ion[2,27]. As a consequence, an enhanced delocalization of non-bonding electron pair of nitrogen is produced, which weakens the N–H bond and allows the hydrogen atom to interact with chloride anion[2,27]. Such interactions will be active in the solution of chitin/DMA–LiCl, because of the presence of

amide group in chitin (Scheme 1). In the case of solutions, these interactions give rise to a macromolecular fluctuating network and then more viscous solution. In the case of chitin–PANI blend film prepared from DMA/LiCl, the miscibility of the blend can be predicted in terms of the interaction of Cl$^-$ ion of chitin with NH of PANI (Scheme 2).

Figure 7 shows SEM photomicrographs of chitin, PANI and P30 blend prepared with varying concentrations of LiCl. In the blends where the ionic strength of LiCl was maintained at 5%, SEM shows homogeneous and continuous structure. However, for blends with a low concentration of LiCl (3.75%) SEM shows homogeneous and fibrous structure. Further, the fibrous structure improves as the percentage of PANI increases in the blend (Figure 8). This result is further supported by AFM study (Figure 9). From the figures, one can observe almost uniform surface and the blends show rough fibrous structure. Even though there is a difference in the morphology of the blend, interaction between chitin and PANI remains the same. The formation of fibrous structure can be explained as follows. During the preparation of the blend, chitin is prepared in DMA with 5% LiCl, whereas EB solution is prepared in DMA. LiCl is responsible for the solubility of chitin in DMA. In other words, DMA acts as a non-solvent for chitin in the absence of LiCl. Therefore, the addition of EB solution to chitin solution is equivalent to the addition of non-solvent to the solution. On the addition of non-solvent to chitin solution, the formation of nano-fibre has been reported in the literature[28]. As the percentage of PANI increases in the solution, effective concentration of LiCl decreases. Hence the solution is on the verge of gelation. This is confirmed from the gelation and aging studies of blend solutions. When a blend solution is exposed to air, the one prepared with less amount of LiCl undergoes gelation more quickly compared to that prepared by maintaining ionic strength 5% LiCl. Also, the gel formation time decreases as the percentage of PANI increases in the solution. Films prepared from the blend solution without maintaining ionic strength, dried at 60°C, show shrinkage, whereas there is no shrinkage in the films prepared from blend solution maintaining ionic strength. Dilute solutions of chitin in DMA/LiCl solvent system form a gel by humidification and a cholesteric

organization of the molecules follows the progressive shrinking of the gel and formation of microfibrils[29]. Further, from ageing studies of the blend, it is observed that blend solutions stored in air-tight containers prepared without maintaining ionic strength undergo gelation within 15–30 days depending on the concentration of PANI in them, whereas the blend solutions prepared with 5% LiCl do not undergo gelation even after six months. In FTIR spectra, the interaction between chitin and PANI is

retained even in the P70 blend prepared without maintaining the ionic strength. The effective concentration of LiCl (1.25%) present in the P70 blend is sufficient for interaction between chitin and PANI. Further, it is seen that even 1.25% LiCl is not required for interaction, as
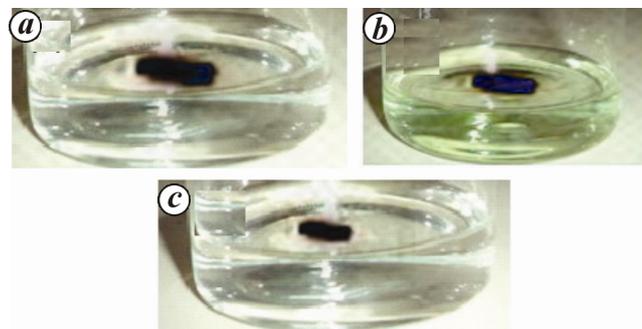

Figure 6. Dissolution study of blend in (*a*) *N,N*-dimethyl acetamide, (*b*) *N,N*-dimethyl formamide and (*c*) *N*-methyl pyrrolidine.
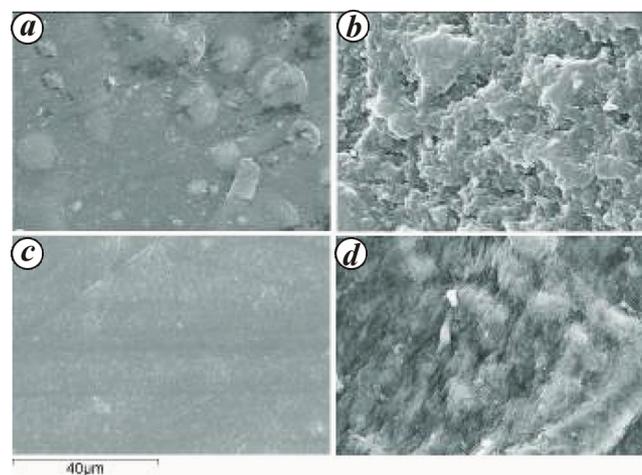
Figure 7. SEM pictures of: *a*, chitin; *b*, polyaniline emeraldine base; *c*, P30 blend with 5% LiCl; *d*, P30 blend with 3.75% LiCl.
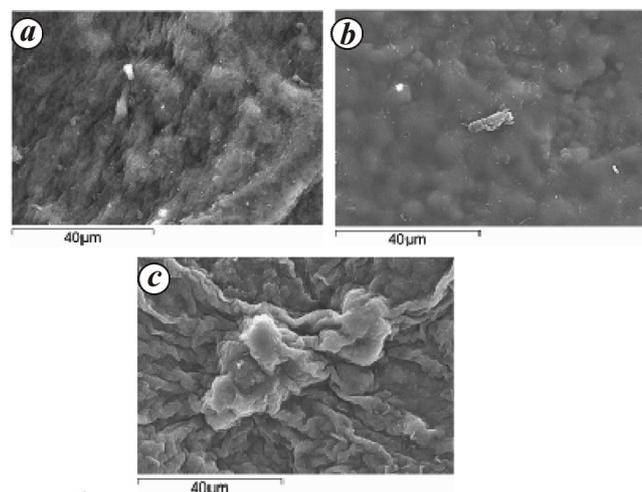

Figure 8. SEM pictures of (*a*) P30, (*b*) P50 and (*c*) P70 without maintaining LiCl concentration.

Figure 5. Fourier transform infrared spectrum of chitin, polyaniline emeraldine base and P30 blend.
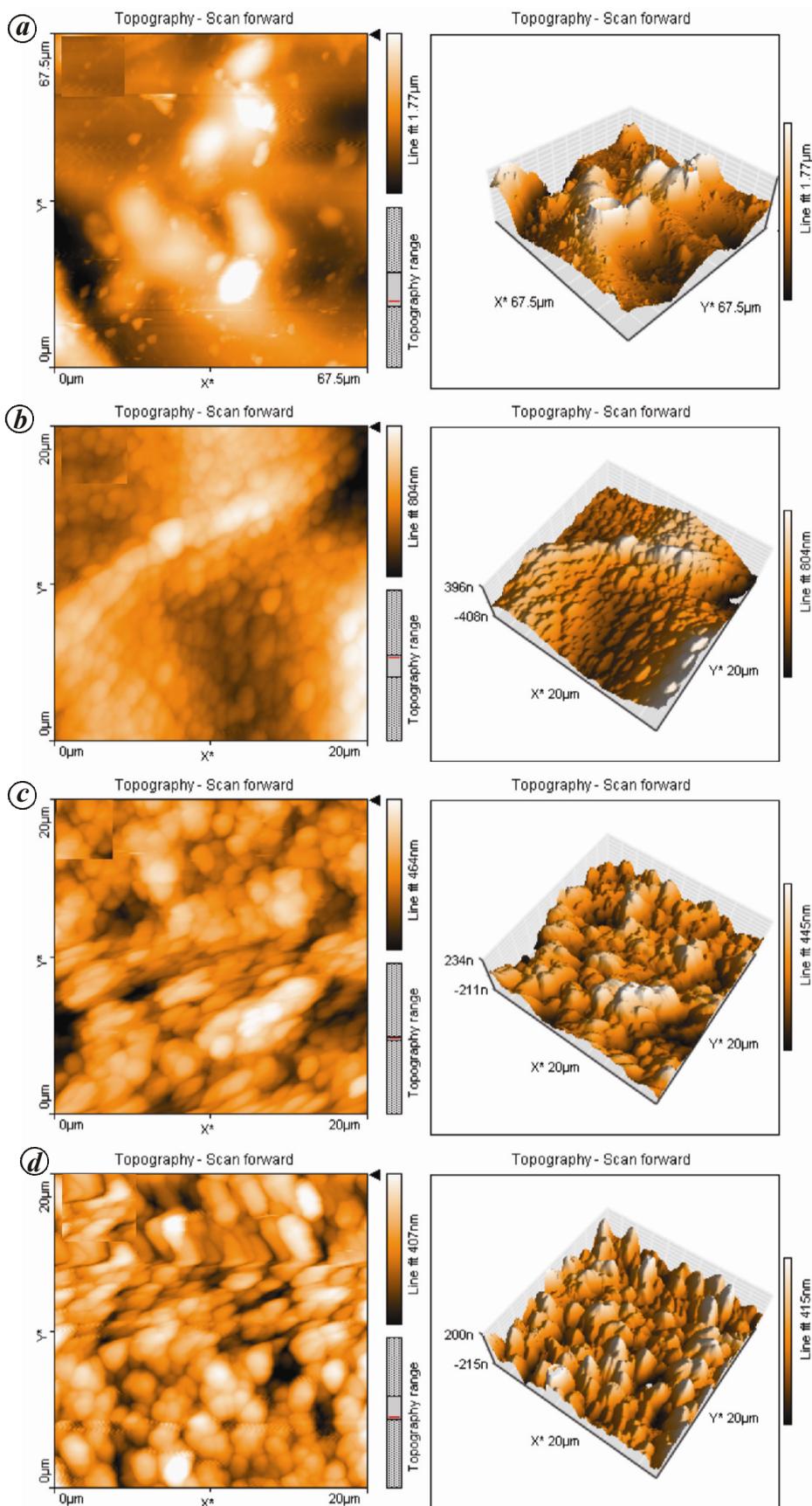
Figure 9. AFM photomicrographs of (*a*) chitin, (*b*) P30 blend, (*c*) P50 blend and (*d*) P70 blend.

we observed LiCl being rejected during film preparation. However, for the preparation of blend solution, 5% LiCl is better as lower percentage leads to gel formation.

Figures 10 and 11 show DSC and TGA thermograms of the blends respectively. The broad endothermic peak between 35°C and 150°C, in DSC is due to the moisture
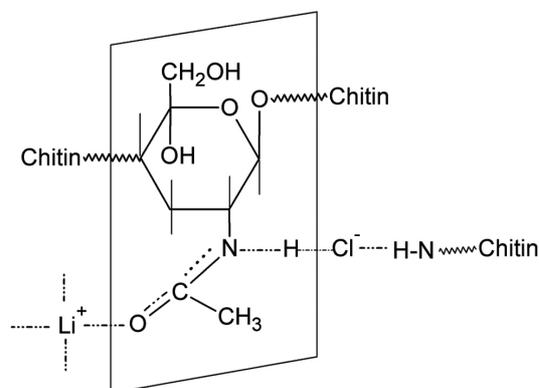
Scheme 1. Interaction of chitin with lithium chloride.
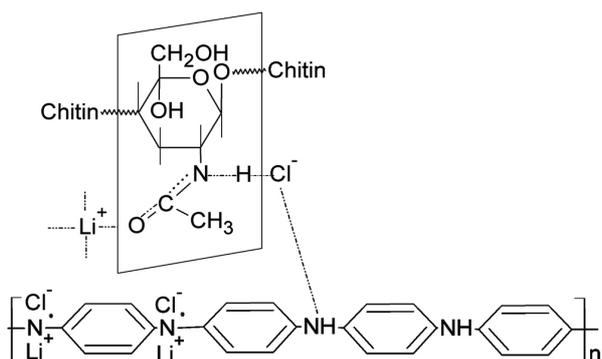
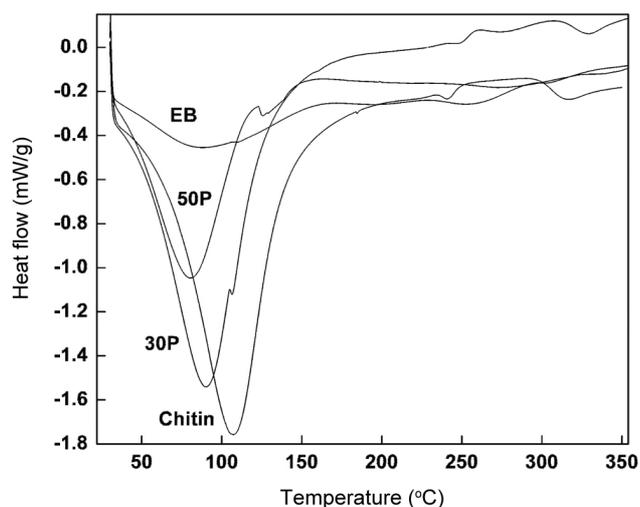**Scheme 2.** Probable interaction between chitin and polyaniline.

Figure 10. Differential scanning calorimetry curves of chitin, EB and its blends.

and bound water present in the sample[30]. This is supported by the initial weight loss in TGA thermograms (Figure 11) and also because weight loss is reduced substantially in this region in the TGA of pre-heated samples[30]. The intensity of the endothermic peak is high for chitin and relatively small for PANI. Polysaccharides usually have a strong affinity for water[31], and in the solid state these macromolecules may have disordered structures which can be easily hydrated. Hence endothermic peak area is large for chitin and small for EB due to poor affinity towards water. Hence water-absorbing capacity of the blend depends on the amount of PANI present in it; as the percentage of PANI increases in the blend, the area under the endothermic peak decreases. No glass transition (T_g) was observed in the present study till 350°C. T_g of chitin is above the decomposition temperature
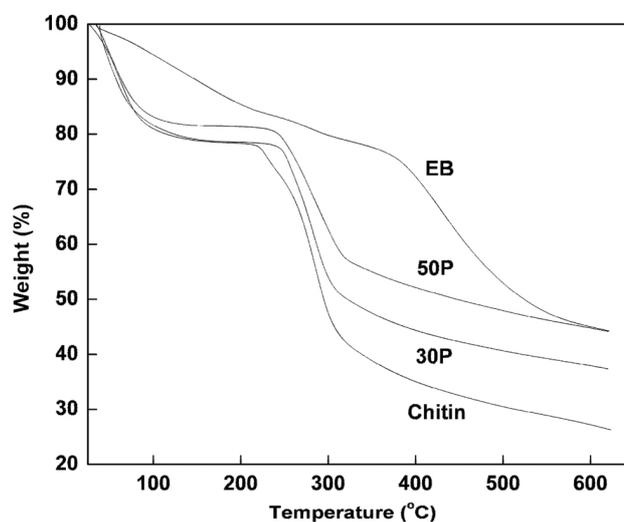

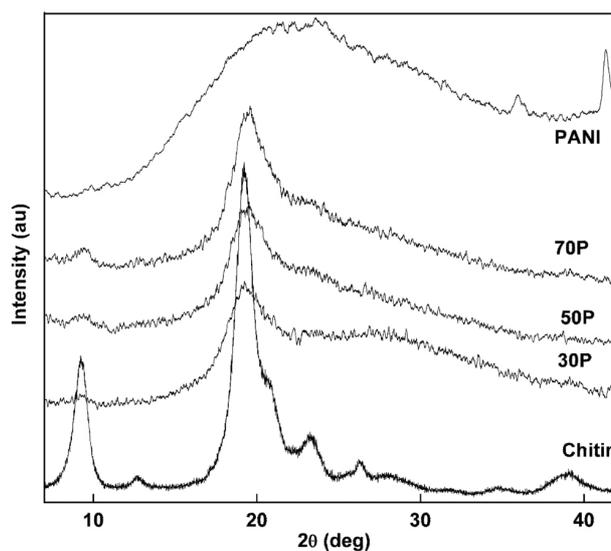**Figure 11.** Thermogravimetric analysis curves of chitin, EB and its blends.

Figure 12. X-ray diffractograms of chitin, emeraldine base and its blends.

(>250°C)[31]. A small endothermic peak near 240°C was observed due to local relaxation of the backbone chain of chitin and not due to T_g (ref. 32). A wide exothermic peak from 260°C to 310°C can be attributed to depolymerization of chitin due to its thermal decomposition, which is supported by TGA results. In the case of chitin–PANI blends, peaks of parental polymers are merged together. The small peak due to local relaxation observed in chitin at 240°C is shifted to higher temperature and area under the peak reduces as the composition of PANI increases in the blend. From TG analysis of the blend, we can see that the weight loss is reduced and degradation temperature is slightly shifted to higher value as the PANI content increases in the blend. This can be attributed to the interaction of the blends.

Figure 12 presents the XRD patterns of chitin, PANI and their blends. Significant peaks of chitin are observed at about 7°, 12°, 19°, 23°, 26° and 39° (ref. 33). A broad amorphous peak at about 23° is observed for PANI. The chitin–PANI blend shows the peak corresponding to chitin at about 19° with reduced intensity due to the addition of amorphous PANI. Since chitin is a crystalline polymer and PANI is an amorphous polymer, as the percentage of PANI increases in the blend, reduction in the intensity of chitin peak at 19° is expected. However, the intensity of the peak at 19° increases as the percentage of PANI increases in the blend. This is due to the interaction between chitin and PANI as explained earlier in the text.

Conclusions

Viscosity measurements of chitin and PANI blends show a linear relationship between intrinsic viscosity and blend composition with a positive deviation from the theoretical value; positive values of Δb refers to the miscibility of the blend system. FTIR analysis further confirms the interaction between chitin and PANI. SEM observations show a homogeneous and continuous structure in the case of blends having 5% LiCl. A homogeneous and fibrillar structure is observed in the case of blends having less than 5% LiCl. Fibrous structure improves as the composition of PANI increases. In the FTIR spectra, the interaction between chitin and PANI is retained even in the P70 blend prepared without maintaining ionic strength. The effective concentration of LiCl (1.25%) present in the P70 blend is sufficient for an interaction between chitin and PANI. This can be further confirmed from the rejection of LiCl in the P70 blend during film casting. This result is supported by DSC, TGA, XRD and dissolution studies of the blends. Finally, it can be concluded that the chitin–PANI blend is miscible for the compositions studied, due to intermolecular interactions.

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