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Interaction of chitosan with polypyrrole in the formation of hybrid biomaterials

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The chemical polymerization of pyrrole in the presence of chitosan has been used to form chitosan–polypyrrole hybrid biomaterials. The hybrids are black in color, indicative of the presence of polypyrrole. FTir, thermogravimetry and scanning electron microscopy verified the presence of chitosan in the hybrids and gave the expected concentration effect. However, FTir, solubility in water and electrical conductivity of the hybrids appear to be contrary to this trend. Hybrids at the opposite ends of the concentration gave similar solubility and electrical behavior while a maxima effect was found for the mid-concentration.

INTRODUCTION

Hybrid biomaterials derived from the interaction of biopolymers with conducting polymers may generate interesting biomaterials that can find applications where charge or electrical conductivity is desirable such as artificial nerves or blood vessels (Valentini *et al.*, 1992; Gott *et al.*, 1961). Previous reports from this laboratory focused on the interaction of collagen with polypyrrole, a conducting polymer, in the production of novel biomaterials (Li & Khor, 1994*a,b*). We showed that with polypyrrole, an intimate polymer blend was formed. When the pyrrole monomer was modified with a pendant ionic group, a collagen–polypyrrole hybrid that gave some indications of interaction between collagen and the conducting polymer, possibly via ionic and hydrogen bonding, was obtained. No doubt future refinements of the substituent on pyrrole with for example, a sulfonyl chloride, will generate the functionality that will lead to direct chemical bonding between the two polymers. Recently, a report on the potential of polypyrrole as a cell growth controller further supports the need to investigate these types of systems (Wong *et al.*, 1994).

An integral part of any study of this nature would be to vary not only the conducting polymer component of the hybrid, but also its biopolymer component. This increases the scope and potentially, the versatility of biopolymer-conducting polymer hybrid systems. Besides collagen, one of the more prominent and readily available biopolymers is chitosan. Chitosan, derived from chitin, extracted primarily from crab and lobster shells has been suggested as a biomaterial for uses which include wound and burn-healing, treatment of dermatitis and fungal infections, for clear and colored soft and hard contact lenses and as a bacteriostat and fungistat (Muzzarelli, 1993). The interaction of chitosan with another conducting polymer, polyaniline, has previously been reported (Yang *et al.*, 1991). The co-polymer enabled polyaniline to be soluble.

Our desire to exploit the advantageous properties of chitosan and polypyrrole has led us to study chitosan–polypyrrole hybrids. We present here the results of this fundamental study that lays the groundwork for deriving a true hybrid with covalent bonding between chitosan and polypyrrole.

MATERIALS AND METHODS

Pyrrole (Aldrich Chemical Co., 99%) was distilled and stored under nitrogen at 4°C prior to use. Chitosan and anhydrous $FeCl_3$ (99%) were obtained from Fluka. All other chemicals were obtained from commercial sources and used as received.

Polypyrrole–chitosan hybrids were prepared by the chemical polymerization of pyrrole in the presence of a 2% chitosan solution in 2% acetic acid using anhydrous $FeCl_3$ (Machida *et al.*, 1989). Typically, appropriate amounts to give 0·1, 0·2, 0·3, 0·4 or 0·5 M of purified

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pyrrole were introduced to the $FeCl_3$ ($FeCl_3$/pyrrole molar ratio of 2·33) containing chitosan solution. The mixture was allowed to stir for 20 min in an external ice-bath and the resultant hybrid was collected using reduced pressure filtration, washed with ether followed by ethanol and vacuum-dried. Controls were obtained from the polymerization of pyrrole in deionized water and 2% acetic acid. In this instance, the resultant precipitates were washed with water and methanol prior to vacuum-drying.

Electrical conductivity measurements were obtained using a Signatone 4-point probe assembly connected to a Keithley 228 voltage/current source and 195A multimeter. Samples were vacuum-dried, pressed into pellets of less than 0·5 mm thickness with a 10 t force. Infrared spectra were obtained on a Perkin Elmer 1600 series Fourier Transform Infrared Spectrometer using KBr discs. Thermogravimetric analyses were performed on powdered samples using a Thermal Analyst 2200 System at a heating rate of 10°C/min. Scanning electron microscopy was performed on a JEOL JSM T330-A scanning microscope on gold coated powder samples.

RESULTS AND DISCUSSION

General

Hybrid biomaterials have been isolated from the polymerization of pyrrole in the presence of chitosan. The black color for all samples prepared testifies to the presence of chemically formed polypyrrole. Samples were sheet-like, becoming more powdery as the concentration of pyrrole used increased. Compared with the controls, hybrids were rough to touch and not readily powdered using mortar and chisel. Powders were eventually obtained with the use of a ball mill grinder. Controls were typical chemically polymerized polypyrrole powders with a soft texture regardless of the initial pyrrole concentration or whether the reaction solvent was water or 0·2% acetic acid.

An interesting observation in this study was the apparent solubility in water of the hybrids. Typically, isolation of chemically formed polypyrrole is by collection of the resultant black precipitate using vacuum filgration on a Buchner funnel. The polypyrrole precipitates are subsequently washed with water to remove residual $FeCl_3$. However, when the collected hybrids were washed with water, they appeared to solubilize to give an intensely black filtrate with no residue left behind on the Buchner funnel. Furthermore, no precipitates could be isolated either by refiltration or centrifugation of the black filtrate. The hybrid precipitates were subsequently washed with ether followed by ethanol to obtain the hybrids.

Additional evaluation of the hybrids' interaction with water was performed by immersing representative samples in distilled water. Two types of behavior were found. The first type, comprising hybrids obtained using 0·1 and 0·2 M pyrrole, gave black solutions when placed in water. Closer observations disclosed that the black solution contained a fine suspension of black particles in the solution. However, no precipitates were obtained after centrifuging. Only when left to stand for 1 week did precipitates appear in these solutions, although the black color persisted. In contrast, the hybrids formed using 0·3, 0·4 and 0·5 M pyrrole concentrations resulted in black solutions that gave precipitates immediately upon centrifuging.

The results suggest first, true hybrids were obtained by the *in situ* chemical polymerization of pyrrole in the presence of chitosan. Second, chitosan probably influences the course of chemical polymerization of pyrrole. A possible explanation may be that at low concentrations of pyrrole (0·1 and 0·2 M), the biopolymer disrupts the steady formation of high molecular weight polypyrrole by its presence. The hybrids so formed are very fine and in water, become fine particulate suspensions. The hybrids derived from the higher concentrations of pyrrole follow a more acceptable trend i.e. are insoluble. This suggests that beyond a certain threshold of pyrrole concentration, chitosan's influence is diminished, probably because chitosan is now comparatively more dilute. In this instance, higher molecular weight polypyrroles are formed, that interact with chitosan to form insoluble hybrids. Last, because of the method of isolation of the hybrids, some low molecular weight polypyrroles are invariably retained and are responsible for the black color in water.

Finally, a pH study of the hybrids gave further insight into the interactions of the two polymers. The pH of the as obtained hybrid solutions (in water) were determined to be in the range of 2 to 3. This low pH is probably attributed to residual $FeCl_3$ which again, is invariably retained by the method of isolation of the hybrids. Adjustment to neutral pH by the addition of NaOH to these solutions should precipitate out chitosan. This is because the NH_3^+ cations on chitosan would be neutralized to NH_2 rendering chitosan insoluble. Indeed, upon addition of NaOH to neutral, the solutions gave fluffy, fibrous-like precipitates. At the higher concentrations (0·4 and 0·5 M hybrids), some separation into black solids and light colored fluff, indicative of chitosan was observed. These observations further substantiate the modes of interaction previously proposed that in low pyrrole concentrations, lower molecular polypyrrole interacts with chitosan to form particulate hybrids. This 'entrapment' of polypyrrole in chitosan is more intimate than on adjustment to neutral pH, when chitosan is expected to precipitate, it does not, preferring to remain in the fine particulate form. At higher

Table 1. Electrical conductivity of chitosan–polypyrrole hybrids

Pyrrole concentration (M)	% Chitosan in hybrid (TGA[a])	Conductivity (S-cm^{-1})		
		Water control	2% acetic acid control	Hybrids
0·1	35·28	—[ab]	—[b]	Not detected
0·2	32·02	35·46	26·25	0·28
0·3	28·92	18·49	37·53	0·86
0·4	23·91	21·21	30·96	2·45
0·5	22·85	20·89	28·65	0·38

[a] Thermogravimetry.
[b] Yield too low to make disc.

concentrations of pyrrole, the high molecular weight polypyrrole is easily dislodged from its interaction with chitosan, resulting in their separation into black solid polypyrrole and chitosan.

Electrical

The electrical conductivity of the hybrids are two orders of magnitude lower than those of the controls (Table 1). It is interesting to note that the conductivity follows a mid-concentration maxima trend, allowing for the non-detection for the 0·1 M hybrid. These results are not surprising considering the more diffused spread of polypyrrole in the presence of chitosan. Furthermore, as has been suggested, lower molecular weight polypyrroles were obtained for the lower concentrations. This would also contribute to a lower conductivity compared with polypyrroles with higher molecular weights, as the shortest polymer has a reduced conjugation system for charge carrier mobility. The 0·5 M hybrid's conductivity is probably due to its distribution in the disc, which is possibly discontinuous, hence its lower conductivity.

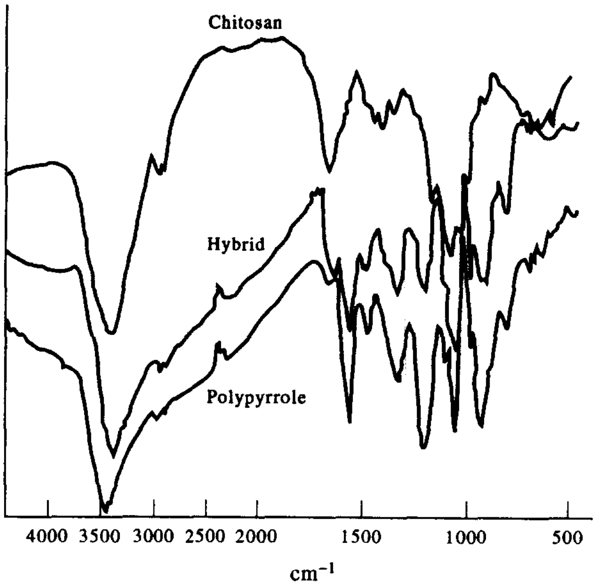


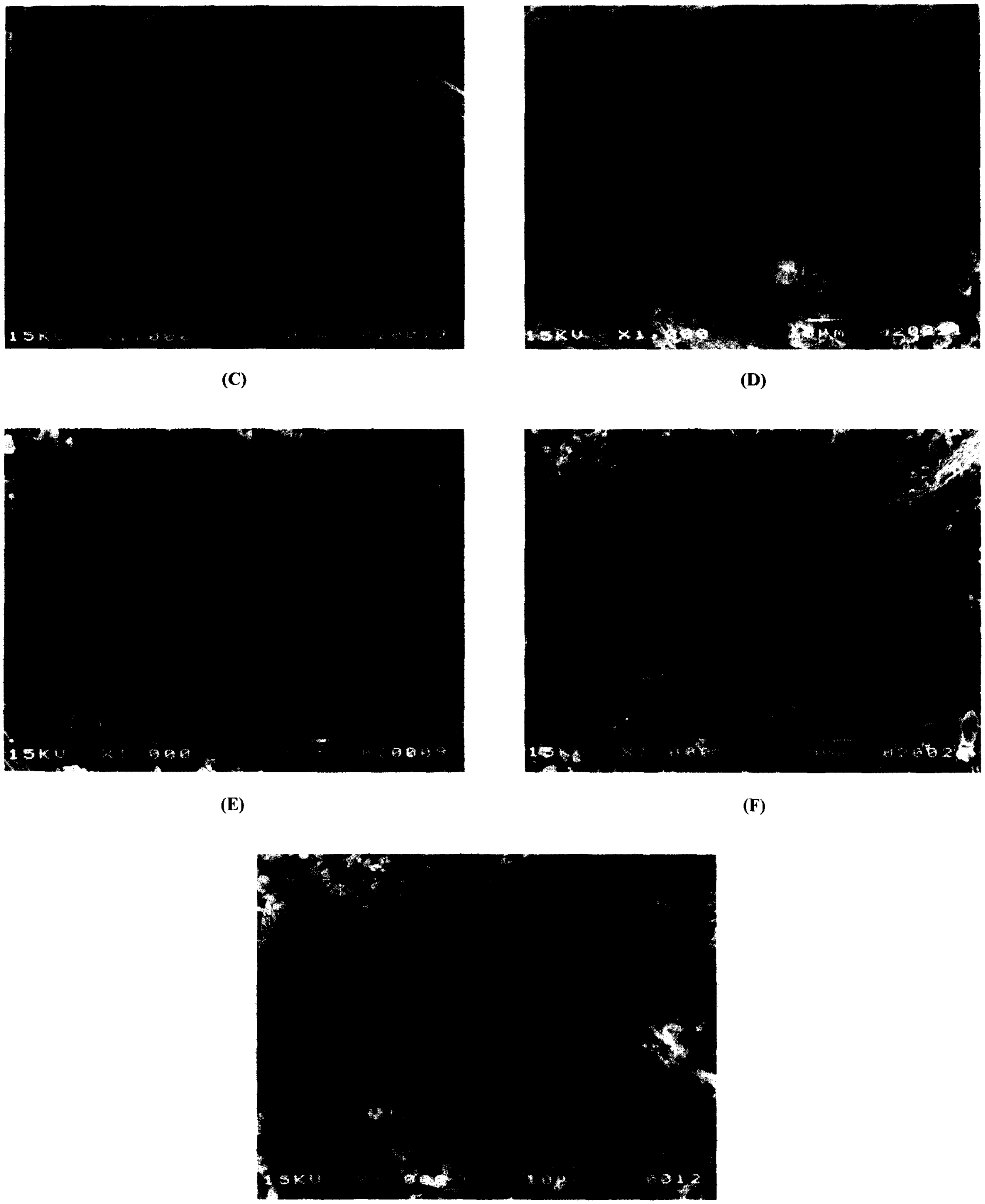
Fig. 1. FTir spectra of chitosan, hybrid and polypyrrole.

FTir and thermogravimetry

The FTir spectra of chitosan, a representative hybrid (0·3 M) and polypyrrole (0·3 M) is presented in Fig. 1. The main features of the spectrum of polypyrrole are two main peaks at 1543 and 919 cm^{-1}. In the case of chitosan, the primary peak is at 1653 cm^{-1}. The spectrum of the hybrid comprised the main peaks of both constituents, and was obtained for all 5 hybrids. There was a concentration dependence found in the hybrid spectra. The main peak for chitosan was higher for the

(A) (B)

Fig. 2. Scanning electron micrographs of polypyrrole–chitosan hybrids. (A) Polypyrrole control: photomicrograph shows the normal grainy features of polypyrrole powder. (B) Chitosan control: photomicrograph shows the sheet-like features of the biopolymer.



(C) (D) (E) (F) (G)

Fig. 2. *Cont.*—(C) 0·1 M photomicrograph shows the hybrid resembles chitosan displaying the sheet-like features of biopolymer. (D) 0·2 M hybrid: photomicrograph begins to show grains of polypyrrole dispersed in over chitosan. (E) 0·3 M hybrid: photomicrograph shows the build-up of polypyrrole grains dispersed over chitosan increasing. (F) 0·4 M hybrid: photomicrograph shows an even higher build-up of polypyrrole grains dispersed over chitosan compared to the 0·3 M hybrid. (G) 0·5 M hybrid: photomicrograph shows the highest build-up of polypyrrole grains and a more intimate association with chitosan.

0·1 M hybrid, decreasing steadily to the 0·5 M hybrid. The reverse for the polypyrrole main peak was also obtained. This concentration is substantiated by similar observations found in the thermograms of hybrids. The decomposition peak of chitosan occurs in the 200–300°C region. The weight loss attributed to chitosan was found to decrease with increasing pyrrole concentration (Table 1). Therefore, FTir and thermogravimetry supports the conclusion that hybrids have been formed and shows an expected concentration effect.

SEM

Scanning electron micrographs are presented in Fig. 2. Figure 2A shows a representative polypyrrole sample obtained from polymerization of a 0·3 M pyrrole in 2% acetic acid. The grainy powdered texture is typical of chemically polymerized polypyrrole. Figure 2B shows the sheet-like structure of chitosan. Figures 2C–G show the micrographs obtained for the hybrids from 0·1 to 0·5 M of pyrrole. This series shows the stark transition from chitosan-like features of the 0·1 M hybrid to the highly speckled grains of the 0·5 M hybrid. The build-up of the grains of polypyrrole and the disappearance of the chitosan features on the surface of the hybrids are quite evident. It is interesting to comment that the SEM data are consistent with results obtained by FTir and thermogravimetry.

CONCLUSION

Chitosan–polypyrrole hybrids have been made. The results are intriguing because data obtained appear to be grouped into two types which are contradictory. Standard characterization methods FTir, thermogravimetry solubility observations and SEM support the expected concentration dependency of the series investigated. However, electrical measurements give rise to a different trend. Further investigations will endeavour to resolve these problems.

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