

Preparation of Poly(vinylidene fluoride)–Polypyrrole Composite Films by Electrochemical Synthesis and Their Properties

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SYNOPSIS

Composite films of poly(vinylidene fluoride–polypyrrole (PVDF–PPy) were prepared by electrochemical polymerization of pyrrole on a very thin PVDF matrix film ($\sim 0.5 \mu\text{m}$). The polymerization was carried out in aqueous media using stainless steel, coated with PVDF matrix, as a working electrode, and *p*-toluene sulfonate (PTS), as a dopant. The films were prepared at different voltages for different durations of time in order to optimize the conditions of composite formation. The resulting films were characterized by studying IR spectra, conductivity, SEM, XRD, and tensile strength measurements. The mechanical properties of the composites were found to have improved, while the conductivity remained more or less same as that of pure PPy. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Electrically conducting polymers have attracted the attention of scientists in recent years because of their many interesting properties with the possibility of application in electronic devices. Polyacetylene has been studied quite extensively and has high electrical conduction when doped.^{1–3} However, it has very poor stability. On the other hand, polyheterocyclics like polypyrrole, polythiophene, etc., exhibit high electrical conduction accompanied by a high stability when exposed to ambient conditions.⁴ Polypyrrole (PPy), however, has poor mechanical properties as indicated by low elongation at break and brittleness.⁵ Attempts have therefore been made in recent years to form a composite material of the conducting polymer with another host polymer matrix. The host polymer is supposed to have good mechanical properties and can be blended easily or can be plasticized. Composite films of PPy with PVC,⁵ PAN,⁶ etc.^{7,8} have been reported.

Poly(vinylidene fluoride) (PVDF) is a ferroelectric polymer, is flexible, and has received wide

attention due to piezoelectric properties. Four crystalline forms of PVDF⁹ have been reported. It was quite interesting, therefore, to make composite films of PPy with PVDF in order to reduce the piezo resistance of PVDF and use it in some devices. The polymer composites have been produced by sorption of liquid or by diffusion of monomer vapors or by solution mixing. However, the electrochemical synthesis offers a new route for synthesizing such composites and has the advantage that the electrical properties of the composite can be controlled by simply varying the conditions of electrolysis. This method also eliminates the need of strong oxidizing agents and hazardous dopants.

In this article, we report the synthesis of PVDF–PPy composite film prepared by electrochemical polymerization of pyrrole on a stainless-steel electrode coated with PVDF matrix film.

EXPERIMENTAL

Materials

Pure PVDF was obtained in the form of granules (Solvay & Cie, SOLEF 1008). Pyrrole (99%) was obtained from Aldrich Chemicals and was distilled

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under vacuum before use. Sodium *p*-toluene sulfonate was obtained from Aldrich Chemicals and was used as received.

Preparation of PVDF-PPY Composites

The electrochemical polymerization of pyrrole was done using a Elico potentiostat Model CL-95. One compartment cell of 50 mL capacity and a three-electrode system was used. The stainless-steel electrode, coated with PVDF, was used as a working electrode, whereas graphite was used as the counter electrode and SCE as reference electrode. The electrolyte was prepared in aqueous media with 0.1M pyrrole with 0.1M *p*-toluene sulfonate (PTS) as a dopant.

The solution of PVDF was prepared by 1% w/v in DMF and heating it to around 70°C for 4 h. A thin film was prepared on a stainless-steel (SS) plate using a Spincoater Model PRS-4000 and subsequently drying it at 75°C for 2 h. The thickness of the PVDF film prepared by this method was approximately 0.5 microns.

The composite films were prepared by diffusion of pyrrole in PVDF films at different voltages such as 0.8, 1, 1.2, and 1.4 V for different durations of time such as 10, 15, 30, and 45 min. The film formed on the SS electrode was washed thoroughly with double-distilled water and then peeled off from the electrode.

Methods of Characterization

The thicknesses of the films were measured by a Baker and Mercer type C-17 meter. Further characterization of PVDF-PPy films was done by studying (1) IR spectra, (2) conductivity, (3) X-ray diffraction, and (4) tensile strength.

1. IR spectra were recorded using a Pye Unicam Model PU 9512.
2. Conductivity measurements were done using a digital four-probe setup Model DFP-2. Through PVDF-PPy film, a certain milli-ampere of current was passed through the outer two probes and the potential difference between the inner two probes was measured at different temperatures. The probe spacing (2 mm) was much larger than the film thickness. Conductivity was calculated using the relation $\sigma = I/V \cdot 2\pi s$ S/cm, where σ is the conductivity; V , the voltage; I , the current; and s , the distance between the probes. Us-

ing these data, the slope of the plot of $\log \sigma$ vs. $1/T$ was used for calculating the band-gap E_g expressed in eV. Occasionally, the conductivity was measured using a two-probe method.¹⁰

3. The X-ray diffraction pattern was recorded using a Philips X-ray generator PW 1729 and automatic diffractometer control PW 1710. A copper K- α_1 line from a copper anode (nickel filter) served as a source of radiation (1.542 Å). The scans were taken at the speed of 1.2 degrees/min in a reflection mode over a range 2θ from 5° to 35°.
4. Tensile strength measurements were done using an Instron Tester Model 1026. The film of width 0.5 cm was gripped between the jaws such that the specimen length was 1 cm and the break occurred in the direction of the machine head which is the longer dimension of the sample. The speed of the head was 5 mm/min. A plot was recorded from which average values of tensile strength and elongation at break could be calculated.

RESULTS AND DISCUSSION

IR Spectroscopy

The electrochemical polymerization of pyrrole on a PVDF-coated SS working electrode gave rise to a flexible black conducting composite film which could be peeled off from the electrode surface easily. To confirm the formation of PPy on the PVDF, the composite was characterized by IR spectra. The IR spectra show a broad absorption band at 3400–3200 cm^{-1} (Fig. 1). It also shows a band at 1540 cm^{-1} due to ring vibrations of PPy. The characteristic bands at 1480 and 1430 cm^{-1} due to C=C and C—N vibrations and at 1080 and 1020 cm^{-1} due to C—H in-plane vibrations have been observed, confirming that PPy has diffused well in the film.

Specific evidence for the formation of a composite can be seen on the basis of IR spectra of PVDF. Absorption bands at 510 and 530 cm^{-1} have been assigned to specific structural conformations of β and α forms of PVDF.¹¹ The ratio of these absorption bands gives an idea about the content of each phase. It was observed during the present investigation that the relative intensity of the band at 530 cm^{-1} increases, revealing the structural transformation to the α form. This is possible only due to the twisting of the backbone chain, which is defi-

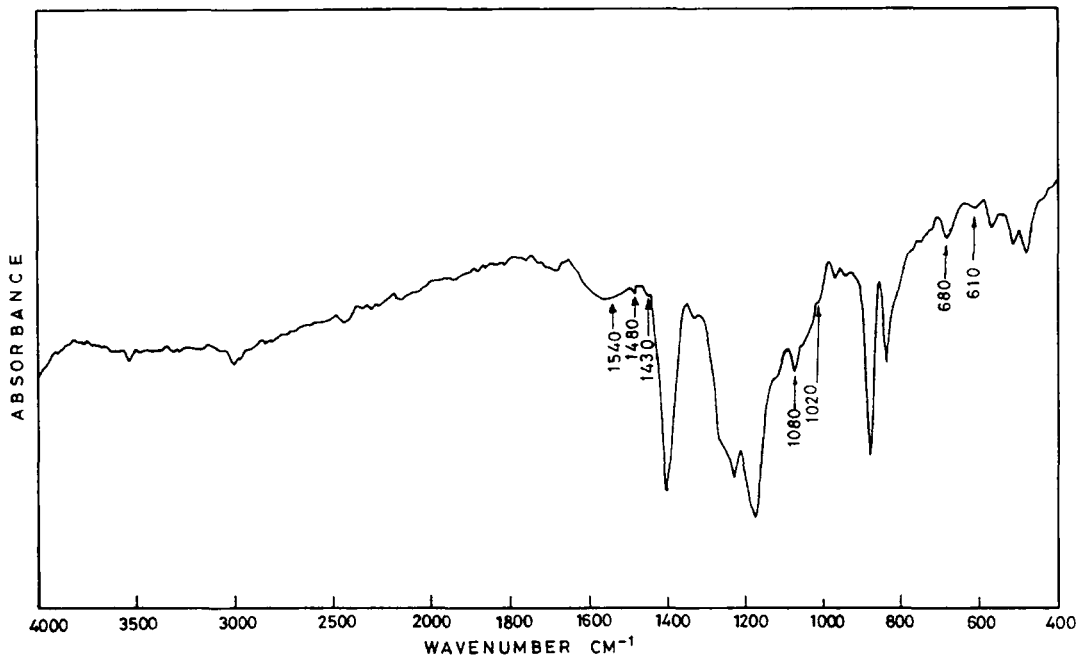


Figure 1 Infrared spectra of PVDF-PPy composite film.

nately caused on account of PPy. Such structural transformations when a composite of PVDF and PPy is formed have been reported.¹²

Thickness Measurement

The thickness of the films was measured under various applied voltages and it was found that the thickness increases initially slowly, followed by a faster rate. The behavior is depicted in Figure 2. It shows that growth depends on voltage and current

density. The current density, on the other hand, is dependent on the concentration of the electrolyte solution.

The change in current with respect to time is shown in Figure 3. It may be seen that at a voltage of 1.2 V the current increases initially and then saturates at about 30 min. The nature of the variation was same at all other voltages except at 1.4 V, where the current slightly decreased after attaining the saturation (not shown in the figure). The role of applied voltage in diffusion and the effective growth of the film is evident from Figure 2. It seems that

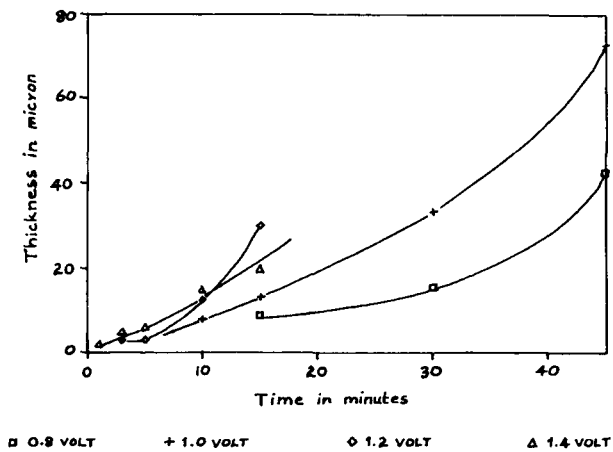


Figure 2 Variation of thickness of PVDF-PPy composite film with time for various applied voltages.

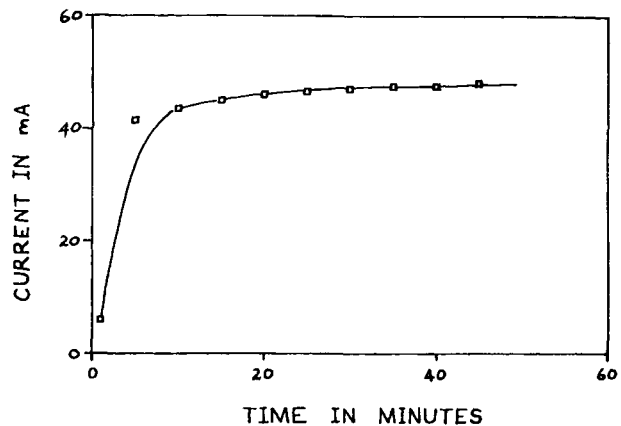


Figure 3 The change in the current with time during formation of PVDF-PPy composite.

as voltage increases (at a constant time) the thickness increases up to a voltage of 1.2 V. A further increase in voltage to 1.4 V for a duration greater than 10 min shows that thickness decreases slightly for the same time of deposition.

Electrical Conductivity

The electrical conductivity of composite films was measured from both sides, i.e., the electrode side and the solution side. It may be seen from Figure 4 that the conductivity increases with the time of polymerization of PPy for films prepared at 1 V.

It was observed that pyrrole diffuses toward the SS electrode and the subsequent diffusion initiates from that side of the PVDF film which is in contact with the SS. The time required for the diffusion of pyrrole throughout the film was found to decrease as the applied voltage increased from 0.8 to 1.2 V. This result shows that it is possible to control the electrical conduction by controlling the polymerization time and voltage.

It is of interest now to see that the conductivity changes with the applied voltage during electrochemical polymerization. The plot of $\log \sigma$ vs. volts (Fig. 5) shows that conductivity increases up to 1.2 V and then decreases. This decrease is possibly due to undesirable side reactions such as ring opening or breaking of the conjugated system which lead to an enhancement of defects and, consequently, lower the conductivity. Similar results have been reported by Satoh et al.¹³ for PPy. Thus, at very low voltages, the reaction rates are low and chains of short conjugation lengths dominate. At slightly higher voltages, the reaction rates are higher and chains of

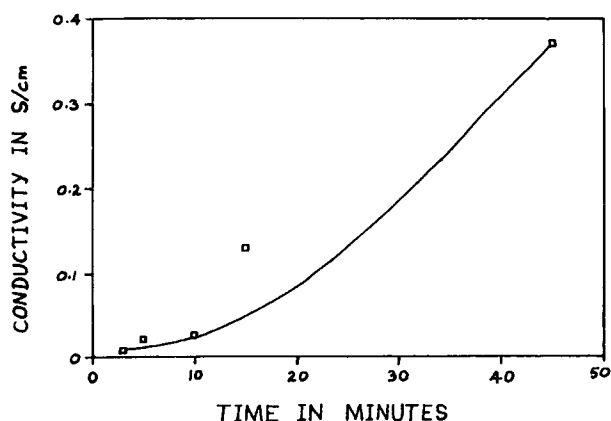


Figure 4 Variation of electrical conductivity with time of synthesis of PVDF-PPy composite. Applied voltage = 1.0 V.

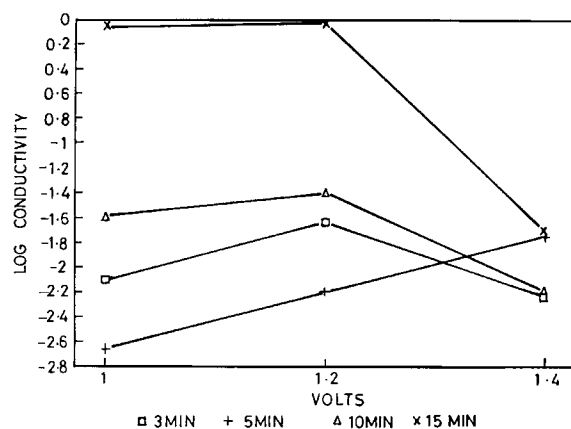


Figure 5 A plot of $\log \sigma$ vs. voltage applied during the synthesis.

longer conjugation lengths increase in number, giving higher conductivity. However, at still higher voltages, the other reactions disrupt the conjugation of the chains and the conductivity decreases. Thus, in the system of our study, it seems that 1.2 V is just optimum when we have a longer conjugation length and fewer defects.

The electrical conductivity of the composite films, measured on both sides, was found to be the same. This supports that the diffusion of pyrrole is uniform throughout the film.

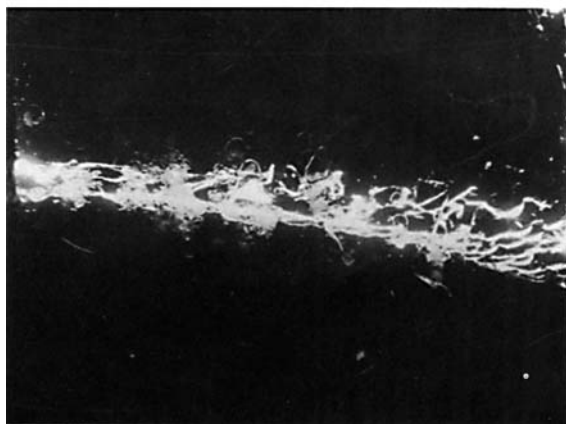
The conductivity of the films were also investigated using the two-probe method at different temperatures. On the basis of these data, conductivity was calculated and also the plot of $\log \sigma$ vs. $1/T$ was plotted. Using these data, the value of the band gap E_g was calculated for pure PPy with the dopant and the (PVDF + PPy) composite, which were found to be .006 and .06 eV, respectively. The low values of E_a indicate that the conduction is electronic in nature. A plot of $\log I$ vs. $\log V$ was constructed for the composite which was prepared at 0.8 V, 15 min. It was seen that the slope of the curve is 1.7 in the low-voltage region and is 2.6 in the high-voltage region. This indicates that the mode of conduction is electronic and is due to the Schottky effect involving traps.

Morphology

The morphology of such films as seen in the SEM is depicted in Figure 6(a). A typical globular structure can be seen for the films prepared under all conditions. A cross-sectional view of the composite film is depicted in Figure 6(b). It shows a uniformly layered structure with some voids in between. On



(a)



(b)

Figure 6 (a) Scanning electron micrograph of PVDF-PPy composite. Note the globular structure. (b) A cross-sectional view of the composite film.

the extreme ends, i.e., on the surfaces of the section, some protruding elongated structures could be seen. These are due to growth of PPy. The uniformity of the structure throughout the thickness suggests homogeneous distribution of pyrrole throughout the film. The cross-sectional views were obtained from the thicker as well as the thinner PVDF films, which were subsequently converted to composites. All such films showed uniform distribution.

Ratio of PPy/PVDF

The weight content of PPy in the composite film was determined from the initial and final weights of the PVDF film. The ratio of weights of PPy to PVDF was calculated to express the PPy content. The PPy content increases with the time of polymerization as well as with the voltage of polymerization except at 1.4 V shown in Figure 7, where there was a slight decrease for higher time.

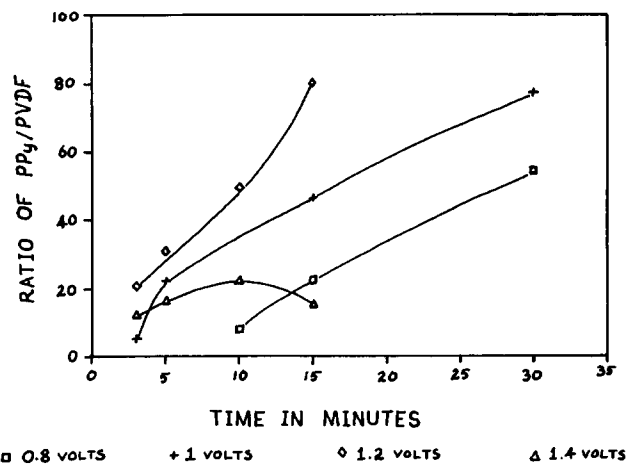


Figure 7 The amount of PPy diffused into PVDF film during electropolymerization expressed as the ratio of PPy/PVDF vs. time of synthesis.

Dependence of conductivity with respect to PPy content in the composite prepared at 1 V is plotted in Figure 8. It may be seen that the conductivity increases with the weight fraction of the PPy.

X-Ray Diffraction

PVDF is a ferroelectric polymer and its crystallization behavior shows that it exists in four different phases: α , β , γ , and δ .⁹ A typical XRD of control PVDF film is shown in Figure 9 (curve A). The assignment of these peaks is also shown. When the film was subsequently doped with PPy, the intensity of these peaks decreased considerably due to composite formation. The % crystallinity obviously decreased when the doping level increased. With a high

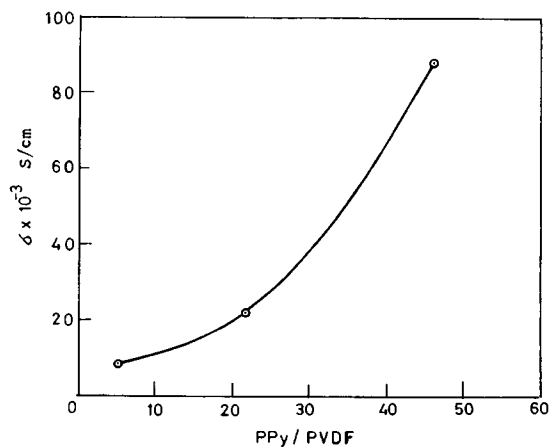


Figure 8 A plot of conductivity σ vs. ratio of PPy/PVDF.

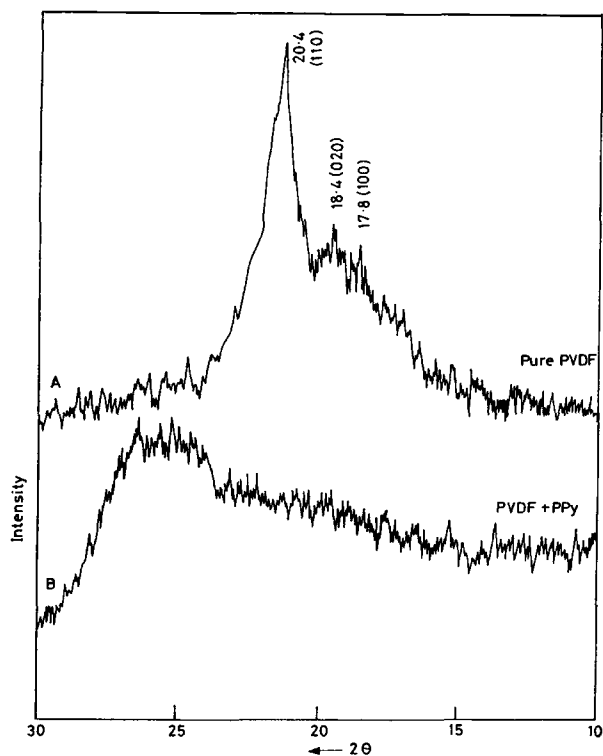


Figure 9 X-ray diffractogram for (A) pure PVDF and (B) PVDF + PPy composite.

level of doping reached, the diffractogram no longer reveals the intense peaks of PVDF, but, rather, a broad hump is seen around $2\theta = 25^\circ$ (curve B). This broad halo is due to the noncrystalline nature of PPy.

Tensile Strength

The mechanical properties of the composite films were measured by studying the stress vs. strain characteristics. The values of tensile strength and % elongation at break for various composites prepared under different conditions were measured. The values for pure PVDF and PPy obtained in this work are comparable to those reported in the literature.⁵ However, the values for PPy are somewhat less than reported, mainly as our samples were prepared in aqueous media and contained PTS as the dopant. It may be seen from Figure 10 that the tensile strength decreases as the PPy content increases for any given applied voltage under which composites were prepared. Similarly, elongation also decreases as the voltage applied during polymerization increases (Fig. 11). These behaviors suggest that there is homogeneous diffusion of PPy in the PVDF ma-

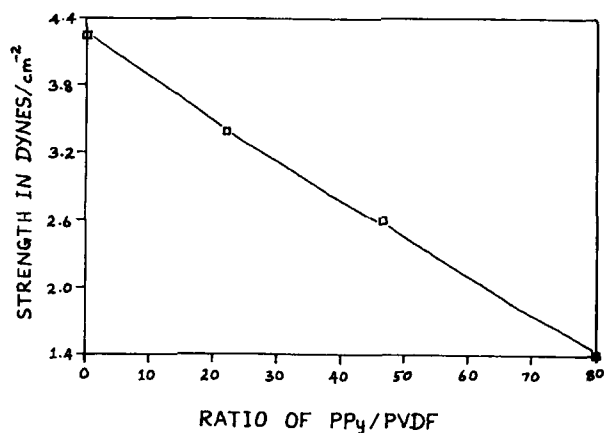


Figure 10 Variation of tensile strength for various composite films (expressed as the ratio of PPy/PVDF).

trix, decreasing the strength. If we recall that strength is determined by the number of tie molecules, it may be concluded that the number of tie molecules decreases or breaks. This can happen only if the interaction of PPy with the PVDF molecule is strong.

CONCLUSION

The present studies thus show that composites of PPy can be prepared with PVDF electrochemically. The diffusion of PPy is homogeneous. The mechanical properties of the composite are improved over pure PPy without decreasing the electrical conductivity appreciably.

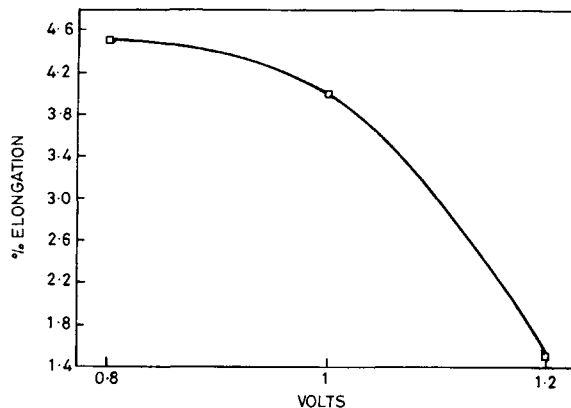


Figure 11 The changes in the percentage elongation vs. voltage applied during electropolymerization of the composite.

The financial support of the Department of Science and Technology (DST) is gratefully acknowledged. P. G. and R. N. wish to thank DST for the award of a fellowship.

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Received November 28, 1994

Accepted June 5, 1995