IN-SITU POLYMERIZATION OF PYRROLE ON COTTON FABRIC TO DEVELOP CONDUCTIVE PROPERTIES

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Abstracts

The present paper reports studies in-situ polymerization of pyrrole on cotton fabric to develop conductive properties. Cotton fabric having plain weave has been treated with ferric chloride as oxidant and pyrrole monomer to produce in situ polypyrrole (Ppy). This polymerization of polypyrrole cotton substrates carried out in water circulating bath for maintaining desired polymerization temperature. The synthesizing parameters which govern the properties of the resulting conductive fabrics such as monomer concentration, oxidant concentration, monomer and oxidant molar ratio, polymerization time, polymerization temperature have been studied. The polypyrrole coated cotton fabrics are also characterized for their electrical, morphology, physical and mechanical properties. The conductivity of the fabric was in the range 10^{-5} to 10^{-1} S/cm. The polymerization temperature of 4°C and polymerization duration of 4h is found to be optimum for the synthesis.

Keywords: Conductive Cotton, Conductive Polymer, polypyrrole.

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1 Introduction

The emerging field of smart textile has attracted an attention of scientist towards electrical conductive fibers. They are now being explored in different applications such as heat generation, electromagnetic interference shielding, electrotherapy, electrostatic discharge protection [1]. Depending on the application, fabrics or yarns may be required to have different levels of conductivity.

Electrically conductive textiles are commonly produced by core-spun method where metallic wires are wrapped with textile fibers, incorporation of conductive fillers or coating with carbon/metal powders, however the metal based conductive textile have the disadvantages of limited mechanical properties like flexibility, heavy weight, corrosion and hence to overcome these shortcomings textile substrates are incorporated with a intrinsically conducting polymer (ICP). Among the intrinsically conducting polymers, polypyrrole has attracted much attention because of its high electrical conductivity, high stability in air with low toxicity and ease of preparation. Textiles provide excellent substrate for depositing conductive polymer because of their high surface to mass ratios, good mechanical performance, resistance to chemicals and harsh environmental conditions, flexibility, and ability to be shaped in various forms and formability to fit end use requirements.

Pyrrole can be polymerized on textiles by chemical polymerization techniques, either by solution and vapor phase polymerization methods. The infusible and insoluble nature of polypyrrole owing to its stronger inter-chain bonding puts severe limitation on its processing. However, it can be deposited onto insulative substrates through in situ polymerization yielding polypyrrole-textile composites. [2, 3].

During polymerization process of the pyrrole monomer with chemical oxidants, such as Ferric Chloride, first an electron is withdrawn from the pyrrole monomer by an oxidant, followed by the formation of two radical pyrrole monomers to a dimer. The electron withdrawing step is repeated at the dimers with the subsequent growing of the chain to polymer, yielding polypyrrole deposited textile substrates [4].

In this study, reactant parameters such as monomer to oxidant ratio and polymerization temperature and time, reactant concentrations were investigated in terms of electrical, physical,

chemical and mechanical properties. The research sought to identify optimized conditions to produce a conducting cotton textile.

2 Materials and Methods

2.1Materials

Commercially desized, scoured and bleached 100% cotton fabric having weight of 120 g/m^2, and plain weave was used as textile substrate. AR grade chemicals such as pyrrole (Spectrochem, India) as monomer and ferric chloride anhydrous (SDFCL, India) as oxidant were used to develop in situ Ppy.

2.2Methods

2.2.1 In situ polymerization of pyrrole

The solutions of Pyrrole and Ferric chloride of desired concentrations were prepared separately, each in 50 ml distilled water. The cotton fabric was treated with $FeCl_3$ solution for 30 minutes. Thereafter, polymerization was initiated by the drop wise addition of pyrrole solution in the same bath with continuous stirring for predetermined time and temperatures. After the completion of treatment fabric samples were removed, washed thoroughly with distilled water and air dried.

2.2.2 Measurement of surface Resistance

The resistance of Ppy coated cotton fabric samples was measured by Digital multimeter Mic 6000Z. From these resistance readings, the resistivity of the Ppy-cotton composites was calculated and the surface resistivity was expressed in terms of electrical conductivity. The conductivity of the resulted composites was expressed in S/cm. The conductivity was computed according to following equation.

$$\rho = \frac{R.t.b}{l}$$

$$\sigma = \frac{1}{\rho}$$

Where, ρ and σ is the resistivity and conductivity of Ppy cotton composites. R, t, b and l be the resistance reading, thickness, width and length of Ppy cotton composite fabrics.

2.2.3 Test methods

The surface morphologies of Ppy coated cotton fabrics were examined using Scanning Electron Microscope (EVO 50).

Tearing strength in warp direction of the fabric samples was measured as per IS 6359: SP-1. The durability of Ppy deposited on cotton fabric against washing was assessed by methods employed for testing the colour fastness to washing ISO 105 - C01 and after the treatment samples were assessed for resistivity.

3 Results and Discussions

The heteroaromatic and extended π-conjugated backbone structure of Ppy provide it with chemical stability and electrical conductivity, respectively. However, the π-conjugated backbone structure is not sufficient to produce appreciable conductivity on its own. Partial charge extraction from Ppy chain is also required, which is achieved by a chemical process referred to as doping. The conductivity of neutral Ppy is remarkably changed from an insulating range to conducting range by doping [5]. An attempt has made to study the effect of reactant pyrrole monomer and ferric chloride as oxidant concentrations with respect to time and temperature with experimental conditions.

3.1 Polymerization Process

Cotton fabric samples were treated with Ferric chloride solution for half an hour followed by drop wise addition of pyrrole solution in the same bath with continuous stirring. The concentrations of pyrrole monomer used were 0.1M, 0.2M, 0.3M and the ratios of Pyrrole monomer to Ferric Chloride oxidant were maintained 1:0.5 and 1:1. In each case the polymerization temperature was varied from 4 to 10°C and time from 2, to 4h.

During the process of the in-situ polymerization, visible changes occur in the color of cotton fabrics. The white surface of fabric turns light green to black gradually, indicating Ppy formation taking place. In case of, 1:0.5 molar ratio of pyrrole to oxidant, the rate of polymerization was found low whereas at higher concentration of oxidant with 1:1 ratio it was

considerably high. Further at lower concentration of pyrrole with 0.1M in bath, with 1:1 ratio, the polymer formation was very minimum. The colour of fabric was light grey.

At lower monomer concentration of 0.1M, the polymerization observed very minimum, whereas, at higher concentration of 0.3M pyrrole, led polymers to be formed in the reaction solutions and on the walls of the reaction vessel. Polymer occurs solely on the surface of the fiber and little quantity was observed in the liquid phase and owing to the larger surface area of the substrates resulted in to superficial deposition.

3.2 Morphological Studies

The SEM images of untreated cotton fabric and Ppy in situ treated sample with 0.3M pyrrole and 1:1 ratio of monomer and oxidant are as shown in fig No. 1 under 5,000 x magnifications. SEM Image (1b) shows a clear surface and deposition of polypyrrole on the cotton fibers. The polymerization of polypyrrole on cotton fabrics takes place through diffusion of polymer inside the fiber bulk as well as the deposition on the fiber surface and the interstices in the fabric [2].

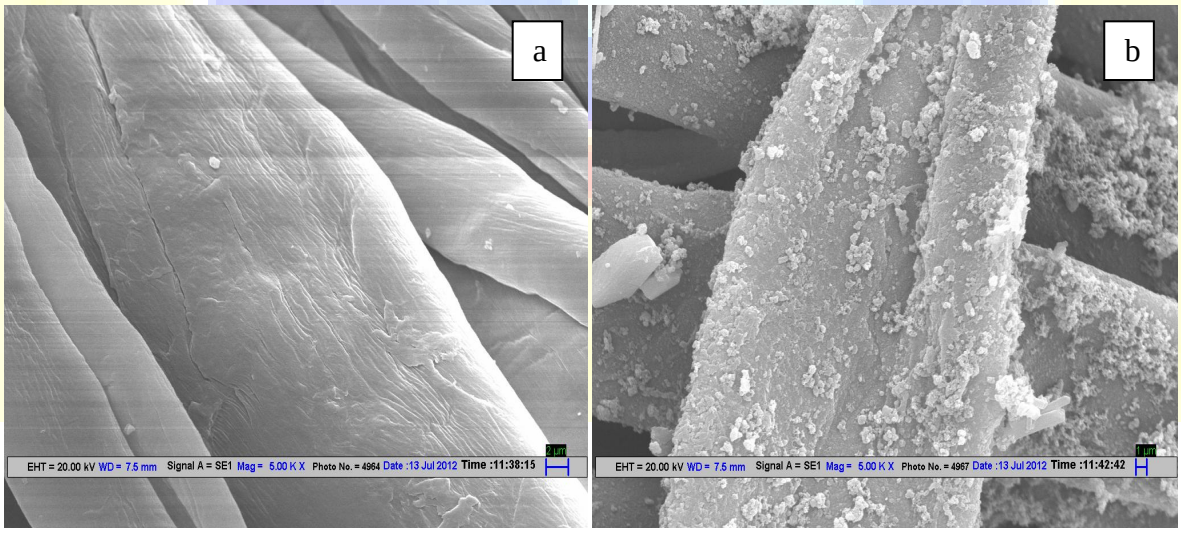

Fig 1: SEM micrographs at 5000x magnification of (a) untreated cotton (b) Polypyrrole deposited cotton fabric

3.3 Effect of monomer and oxidant ratio

Along with oxidation required for polymerization, ferric chloride supports for conductivity by provides negative species known as dopant for Ppy. The concentration of pyrrole used for polymerization from 0.1M to 0.3M as pyrrole to oxidant molar ratio was varied as 1:0.5 and 1:1. The treated material is tested for resistivity and calculated conductivity is plotted against monomer concentration as shown in fig 2.

At 1:0.5 ratio of pyrrole to oxidant conductivity is very low as found to be 0.675 S/cm at higher concentration 0.3M was studied. At the same concentration of pyrrole with 1:1 ratio of pyrrole to oxidant, conductivity observed was 1.87 S/cm which is significantly high. The oxidant concentration is very important to achieve high conductivity with manipulating its concentration one can control the conductivity.

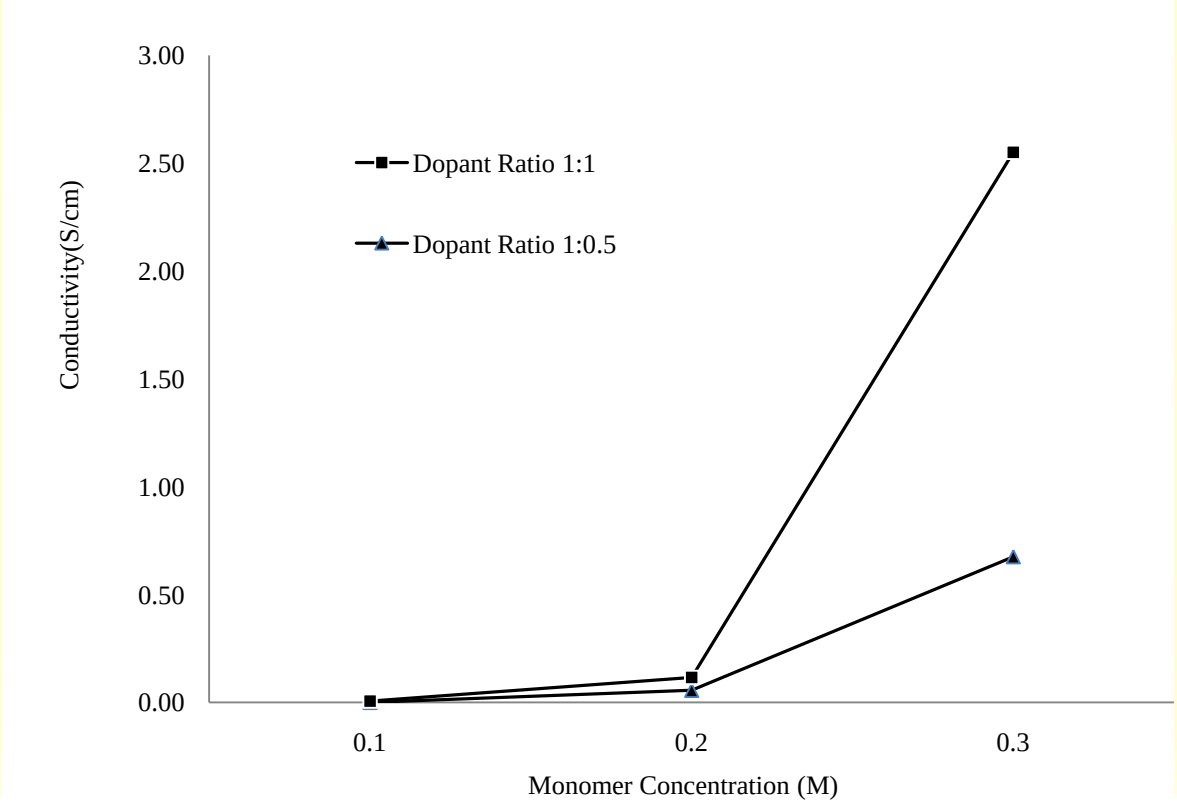

Fig 2 Effect of pyrrole to oxidant ratio on conductivity

At lower concentration of pyrrole monomer, the deposition of Ppy on the cotton fabric produces a thin coating layer with high resistivity. As the monomer concentration increases, the coated substrates thicken by allowing more Ppy to deposit on to the fiber surface. But there are limitations for improving the conductivity of heavily coated textiles. Thicker Ppy coated sample

when tried at 0.4M or more pyrrole concentrations found stiffer. Hence maximum up to 0.3M pyrrole concentrations with given experimental conditions resulted smooth surface and flexible substrates.

Oxidant concentrations play important role in conductivity of cotton fabric as it initiates the polymerization process and polymer obtained is in conducting form. By increasing the ferric chloride concentration, there is an increase in conductivity by providing dopants.

3.4 Effect of Polymerization Temperature

The polymerization was carried out at three different temperatures viz 4, 6 and 10°C. The conductivity of in situ Ppy treated cotton fabric samples are plotted against monomer concentrations as shown in fig. No 3.

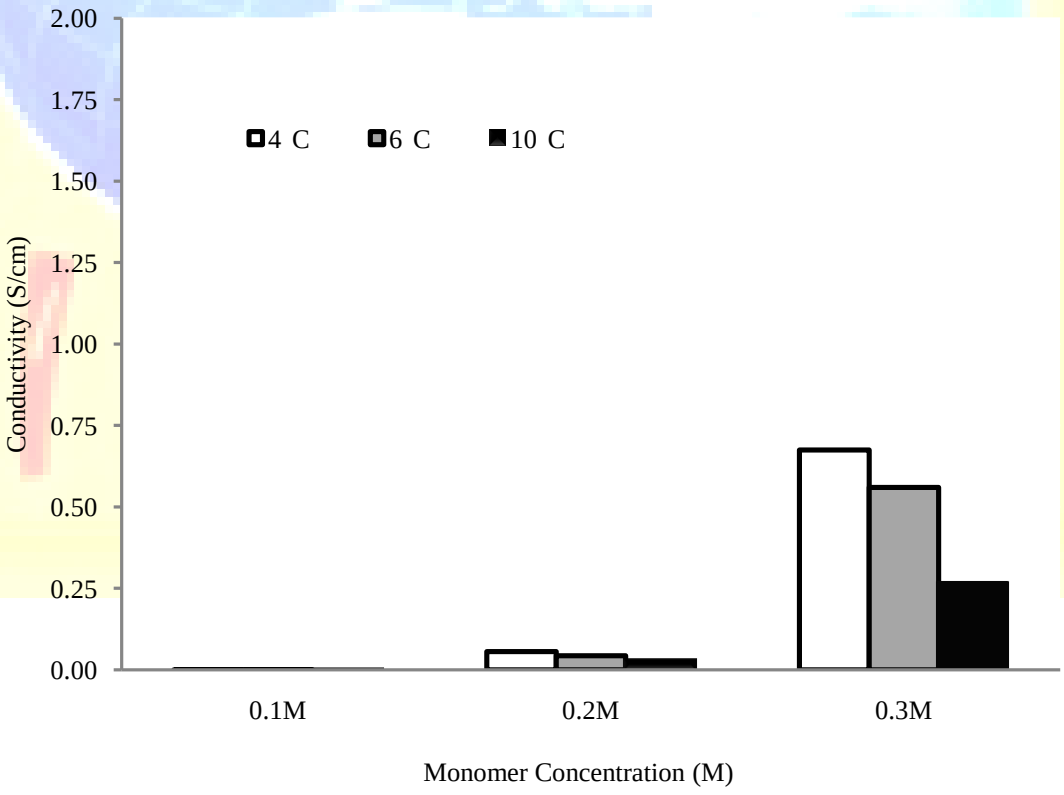

Fig 3 (a) Conductivity of polypyrrole composites developed with monomer and oxidant ratio of 1:0.5 at different Polymerization temperature

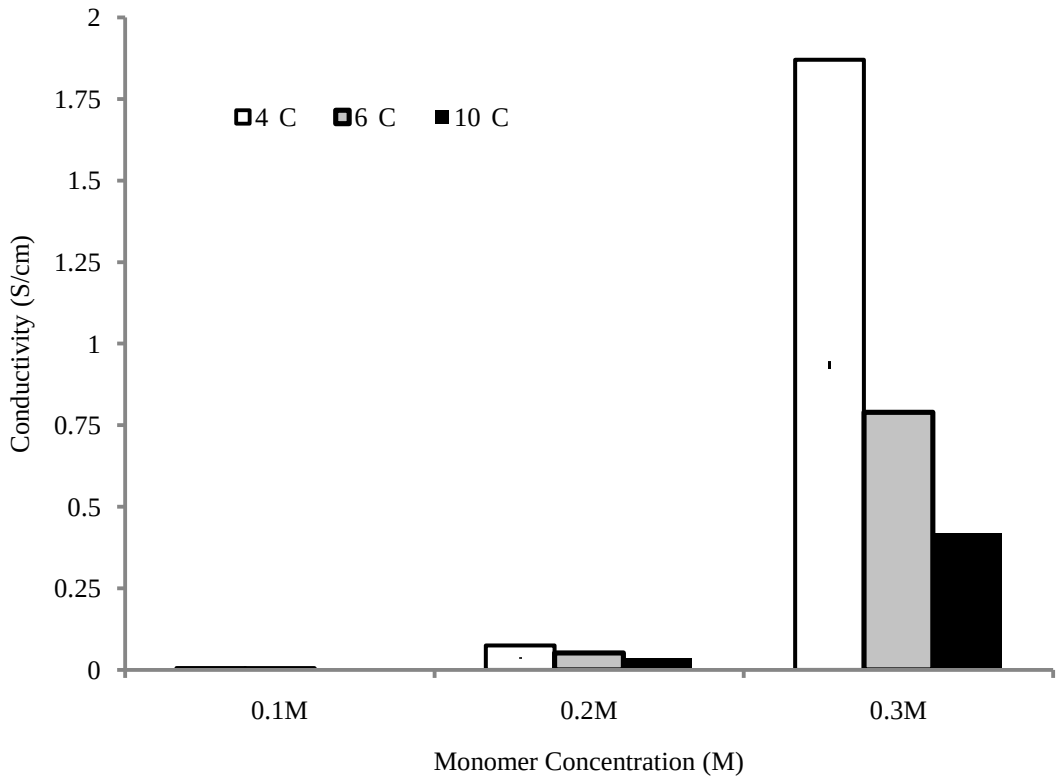

Fig 3 (b) Conductivity of polypyrrole composites developed with monomer and oxidant ratio of 1:1 at different Polymerization temperature

From the fig. No 3 a and b, it is clear that the polymerization temperature increases, the conductivity of in situ Ppy cotton fabric decreases. Polymerization of pyrrole mainly occurs at α carbon which is the ideal Ppy chain formation with linear and planer orientation of pyrrole moieties along the main chain [5, 7].

Higher conductivities at lower temperature are generally attributed to an increase in the number of defects of the polymer structure when it is obtained at higher temperature. These defects break the delocalization through the π- system. The low temperature seems to promote an orderly growth of chains with a greater conjugation and smaller amount of defects [1]. Hence the low temperature polymerization of pyrrole on surface of fabrics was helpful for obtaining thinner coatings resulting in more adherent film and more ordered structures of Ppy with higher conductivity. Hence the conductivity is more at 4°C compared to higher temperatures.

3.5 Effect of Polymerization Time

The polymerization reaction was carried out for four hours with the interval of 1 hour. The conductivity achieved with respect to time has compared and represented in fig 4 a and b.

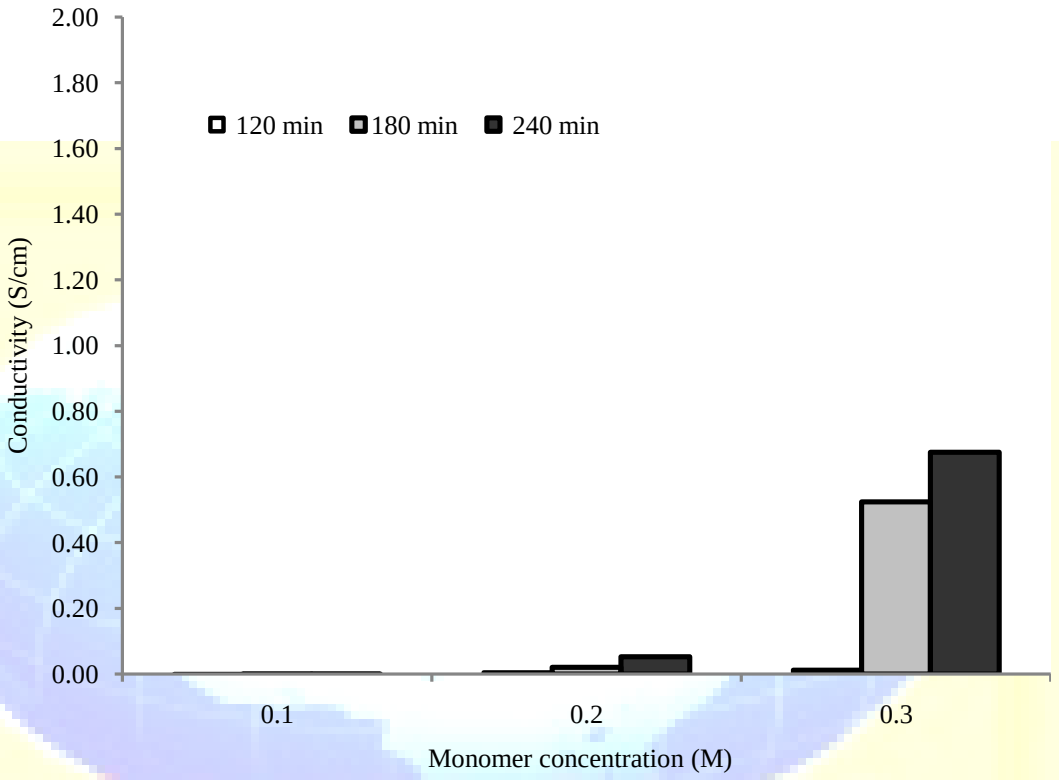

Fig 4 (a) Conductivity of Ppy cotton composite at various duration of polymerization with monomer to oxidant ratio of 1:0.5

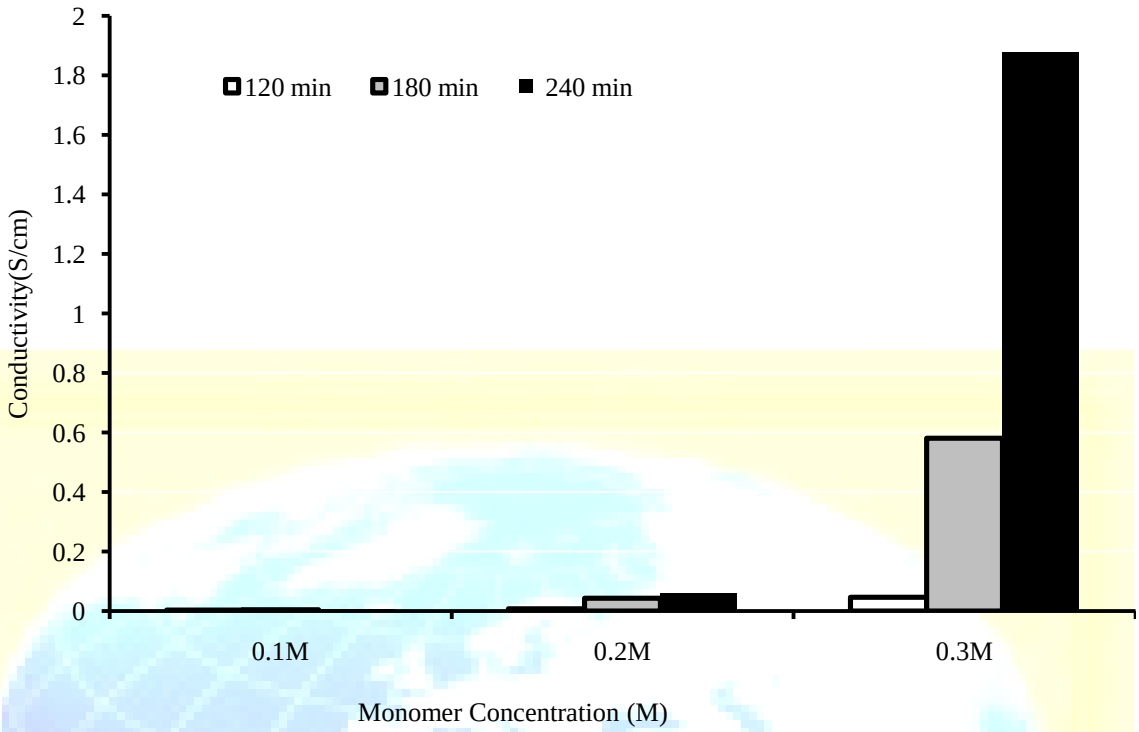

Fig 4 (b) Conductivity of Ppy cotton composite at various duration of polymerization with monomer to oxidant ratio of 1:1

Fig 4 a and b shows that, the exponentially increase in conductivity of composites with increase in polymerization time. With low polymerization time of 2 hours, the fabric appeared grey in color for all the concentrations studied which shows that this duration is not sufficient for the penetration of the Ppy inside the fabric, and also it does not allow the growth of polymer chain, thereby giving low conductivity. After the polymerization time for 4 hours, the dark black colour developed on the fabric surface which means that sufficient polymerization and deposition of Ppy on substrate. Longer deposition time promotes the uniform deposition of Ppy on the surface which also enhances the conductivity. The polymerization time 4 h was showed higher conductivity than the 2 and 3h.

3.6 Tearing Strength

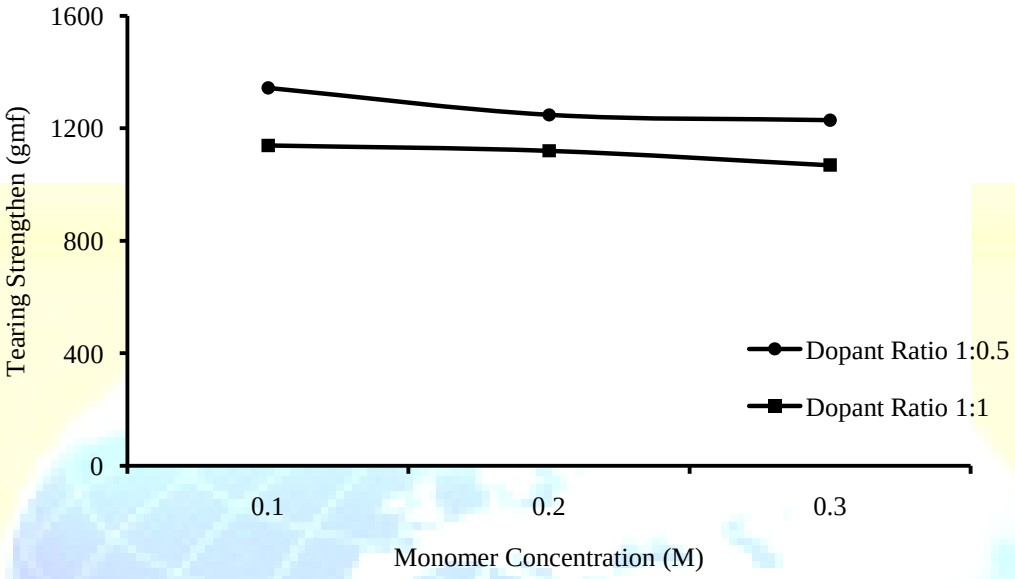

Fig 5 Effect of monomer to oxidant ratio on tearing strength

Due to the higher monomer and oxidant molar ratio, the deposition of Ppy on the cotton fabric is more and Ppy is penetrated into the fabric structure which restricts the yarn movement in the fabric during tearing. Hence the monomer to oxidant ratio 1:1, gives less tearing strength than the ratio of 1:0.5. Figure 5 shows that increase in monomer : oxidant ratio as well as monomer concentration, affects the tearing strength of fabric as compared with the controlled cotton fabric tearing strength 1785.6 gmf. The polymerization carried out at 0.1M concentration of pyrrole has not resulted in significant reduction in strength. However at higher concentrations of pyrrole from 0.2M to 0.3M, it decreases to 20-30% at all the three duration of polymerization. This can be attributed to the low pH value of polymerization reactants which reduces the strength of cotton during treatment. Oxidant concentration mainly affected the tearing strength of cotton fabric because ferric chloride oxidized the cellulose structure with longer polymerization time and thereby reducing the strength of cellulose more effectively in the polymerization process [4].

3.7 Durability to Washing

The advantage of conductive textile material lies in its flexibility, formability in smart clothing where these materials may undergo washing or laundering. Therefore, conductivity of the samples is tested after washing. The method followed for washing was same as method intended to study the colour fastness to washing with ISO 105 C01 followed by rinse and dry. After the washing it was observed that the conductivity of the material was reduced drastically to about 25% as the loosely bonded Ppy gets removed from the surface of substrate. Further, the loss in conductivity by washing is reported mainly due to anion de doping [7].

4 Conclusions

The electrically conductive textiles are turning towards for most of envisaged applications due to their flexibility, light weight, environmental stability and ease of application. The highest conductivity is obtained when the pyrrole is polymerized in situ on cotton substrate with 0.3M concentration and equal mole of ferric chloride as oxidant at 4°C for 4 hours. SEM showed the clear surface and deposition of polypyrrole on the cotton fibers which gives the conductivity of in situ Ppy cotton fabric. Mechanical strength loss and decrease in conductivity after washing remained drawbacks of this conductive material.

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