Studies on Increasing Conductivity of Polyurethane Films and Nanofibers

M. Yanılmaz, H. Karakaş, A. Sezai Saraç and F. Kalaoğlu

***Abstract*—There is a growing interest in development of textiles with electrical conductivity due to the variety of applications including electromagnetic interference shielding, electrostatic dissipating, antistatic applications, microwave reduction, gas sensors, biomechanical sensors. Polypyrrole is one of the most promising conductive polymers due to its high electrical conductivity and good chemical stability, however it has some drawbacks such as poor processability. In this paper, production of nanofibers of Polyurethane by using polypyrrole was studied. Films and nanofibers of PU-PPy were successfully prepared for the purpose of combining the properties of polyurethane with polypyrrole. The effects of polypyrrole content on thermal, mechanical, dielectric and morphological properties of the composites were investigated by using Dynamic Mechanical Analyzer (DMA), Dielectric Spectrometer, UV – Vis spectrophotometer and the Scanning Electron Microscope (SEM).**

***Index Terms*—electrospinning, nanofiber, conductive fiber, polypryrrole, polyurethane**

I. INTRODUCTION

In recent years, efforts on new developments in textiles have focused on new application and property possibilities. Electrical conductivity in textiles is among the most out coming properties that have been studied. Conductive textiles have numerous applications including electromagnetic interference shielding, electrostatic dissipating, antistatic applications, gas sensors, flooring, microwave reduction, biochemical sensors, heating devices and electrostatic dissipating. These materials find applications also in military use [1]-[4]. Conducting polymers have attracted much attention due to their excellent electrical, electrochemical and optical properties, however as they have poor processability and stability, their usage has been restricted [5]. Among conducting polymers, polypyrrole (PPy) is one of the most important one as it is highly conductive, stable and relatively easy to synthesize. However, its poor mechanical properties and processability limit its practical use [6]-[8]. Polyurethane (PU) is an outstanding material used in textile applications. Polyurethane has wide range of textile applications and additionally it can be applied to waterproof-breathable fabrics, synthetic leather, antishrink wool, military textiles, adhesives and fine chemicals [9]. Furthermore, combining ordinary fabrics with semi-conductive polyurethane films can lead to the development of smart textiles.

In this study, it was aimed to produce conductive films and also conductive nanofibers. Nanofibers were produced by the electrospinning method. Electrospinning is an easy method to obtain micro and nanofibers through the action of electrostatic forces [10-12]. The nanofibers obtained have a high surface to volume ratio, high surface energy, high surface reactivity and high thermal and electrical conductivity [13-14].

II. EXPERIMENTAL

A. *Materials and Chemicals*

Thermoplastic polyurethane was taken from Flokser Co. (Istanbul, Turkey) with a molecular weight of 75,000 (GPC result). The solid content of PU was 35 wt. % in dimethyl formamide (DMF). Pyrrole (C_4H_5N, Aldrich Co. Ltd., analytical), Dimethylformamide (DMF, $(CH_3)_2NC(O)H$, Riedel-de Haen, analytical), ceric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$, CAN, BDH analytical), methanol (technical) and ethanol (technical) were used.

B. *Preparation of PU/PPy Composites and nanofibers*

Polyurethane/polypyrrole composites were prepared using chemical oxidative polymerization of pyrrole in polyurethane matrix with three components. Homogeneous composite films were obtained by solution casting method. Firstly polyurethane was dissolved in DMF. A calculated amount of pyrrole monomers were added to the definitive volume of polymer solution and stirred until homogeneous solution was obtained. Ceric ammonium nitrate (CAN), used as an oxidizing agent, was added into the solution which included PU and pyrrole monomers. Polymerization of pyrrole immediately occurred at room temperature. Excess solvent was evaporated by applying heat to obtain homogenous and viscous solution. Then the solution was poured onto a glass plate and allowed to dry in a vacuum oven for 1 day at 80ºC. The black PU/PPy composite films were removed from glass plate and washed with ethanol. Composite films were prepared by using a three-component system, so weight of pyrrole amount was calculated and reported according to pyrrole percentage of the three components.

PU/PPy nanofibers were produced by the electrospinning device. The electrospinning apparatus consists of a syringe pump, a high-voltage direct current (DC) power supplier

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generating positive DC voltage up to 30 kV and a grounded collector that was covered with aluminum foil. The solution was loaded into a syringe and a positive electrode was clipped onto the syringe needle, having an outer diameter of 0.8 mm. The feeding rate of the polymer solution was controlled by a syringe pump and the solutions were electrospun onto the collector. The syringe pump was set at a volume flow rate of 2 ml/h, the applied voltage was 15kV, tip-to-collector distance was 10 cm, all solution preparations and electrospinning were carried out at room temperature. For preparing electrospinning solutions, 2 g PU was dissolved in DMF and THF (tetrahydrofuran) mixture (v/v: 1/1). A controlled amount of pyrrole monomers was added to the solution. Composite solutions having a different ratio of pyrrole monomers were prepared with 20% (w/v) in the solvent mixture. Then, Ce(IV) was added to this solution.

C. Characterization

UV – Vis Perkin Elmer Lambda 45 spectrophotometer was used for UV/vis measurements. The AC measurements were performed using Novocontrol Broadband Dielectric Spectrometer (Alpha-A High Performance Frequency Analyzer, frequency domain 0.001Hz to 3GHz). SEN-3000M model Mini-SEM was used for nanofiber images.

III. RESULTS AND DISCUSSION

For the detection of PPy , composite films treated with methanol. The UV/vis spectra of the PPy extracted by methanol from composte films are shown in Figure 1. The peak at 460 and 560 nm correspond to PPy, PPy of higher molecular weight and radical cations. The very well defined and sharp peak observed at 460 nm indicates that molecular weight of the PPy has a narrow distribution. For all composites, the absorption intensity around 466 nm increases with the increasing content of PPy [15-19].

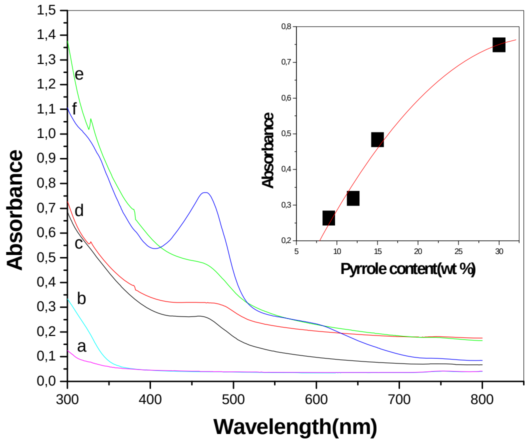

Fig. 1. UV/vis spectra of PPy extracted from PU/PPy composite films by methanol.(a. pyrrole monomer, b. CAN, c. 9%, d. 12%, e. 15%, f. 31% pyrrole).

The electrical conductivity of the composites depends on the extent of dispersion, geometry and interactions of the components [20]. The influence of the amount of PPy in PU/PPy composites on their electrical conductivity was investigated. The room temperature conductivity of PU/PPy composites are shown in Fig 2. The conductivity of the composites increased with increase in pyrrole content. The conductivity of an order of 10^{-5} S/cm was obtained in a PU/PPy composite containing 23 wt.% of pyrrole . Also, in Fig 2, we see the conductivity of composites increases with increasing PPy peaks in UV-Vis spectra. It is a proof that conductive component increases in the structure.

The dielectric constant of a material depends upon the polarizability of the molecules. The figure represents the effect of initially added pyrrole on the dielectric constant values of PU matrix. It can be seen that the dielectric constant increases with pyrrole loading at low frequencies. Another observation is that the dielectric constant values decrease with increase in frequency for all samples. It was also observed that dielectric constant decreases with increase in frequency, which can be attributed to increase in orientation polarization.

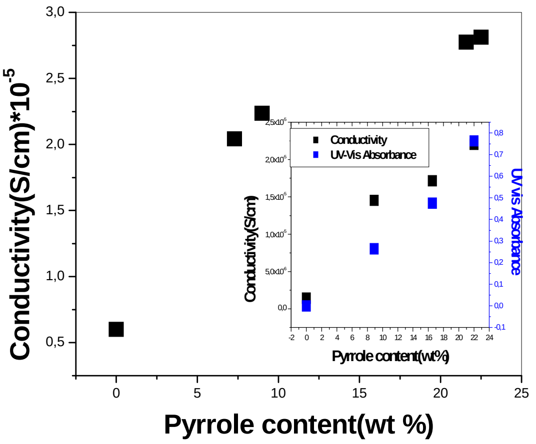

Fig. 2. Conductivity of PU/PPy composites (at 10^7 Hertz) versus pyrrole content in the composites and conductivity and UV- vis absorbance changes versus pyrrole content

The mechanical properties of the composites may depend on the relative concentration of the two phases, the nature of the disperse phase, surface characteristics, distribution pattern, domain size and shape and degree of compatibility. The stress–strain profiles are illustrated in Figure 3. Stress–strain curves for all of the polyurethane composites showed the elastomeric behavior of typical polyurethanes [21]. It can be seen that the higher PPy content stronger the modulus. Therefore, as compared to the neat PU, the PPy-containing polyurethane composites are more rigid. In addition, the more brittle behavior of the PPy-containing polyurethane composites is attributed to more phase mixing present in these samples.

Also, it can be noted that the introduction of PPy can improve the modulus due to rigidity of polypyrrole chains [21]. This high performance of the composite is attributed to a homogeneous dispersion of PPy in the matrix as well as to the strong interfacial interaction between the PPy, Ce(III) and PU matrix [20]. The SEM images of electrospun nanofibers can be seen in Figure 4.

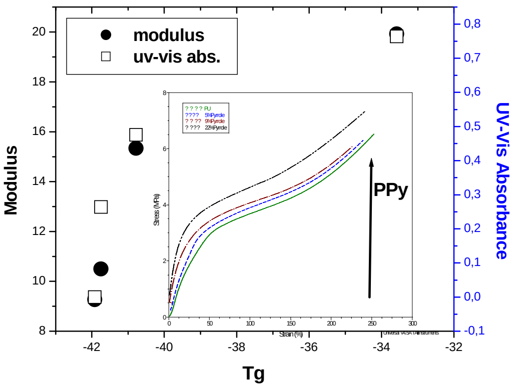

Fig. 3. Stress strain curves of the composites with included different amounts of pyrrole and increasing of Modulus, Tg and UV-Vis Absorbance values change due to pyrrole content

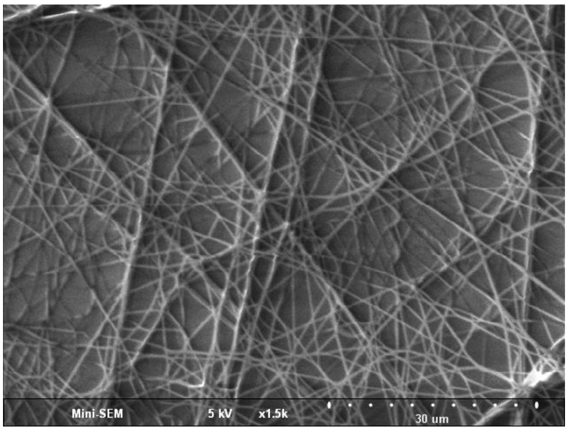

Fig. 4. SEM images of electrospun PU/PPY nanofiber

IV. CONCLUSIONS

The oxidative matrix polymerization of pyrrole by CAN in the presence of polyurethane has been studied. We have observed a very homogeneous polymerization in PU matrix due to strong oxidation power of CAN. UV-Vis spectroscopic studies confirm the existence of PPy chains in the polymer that attributes to the absorption change by changing pyrrole content. When PPy were incorporated into the polymer composites, higher modulus was obtained due to the lower degree of phase separation. Enhanced phase mixing can be explained by electrostatic interactions of the polyurethane with oxidizing agents and polypyrrole in the composites. The conductivity of the composites increased with increase in PPy content. The conductivity of an order of 10^{-5} S/cm was obtained in a PU/PPy composite containing 20 wt. % of pyrrole.

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