(REFEREED RESEARCH)

EFFECTS OF POLYPYRROLE ON THE CHARACTERISTICS OF POLYURETHANE BASED COMPOSITES

POLİPİROLÜN POLİÜRETAN ESASLI KOMPOZİTLERİN ÖZELLİKLERİNE ETKİSİ

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ABSTRACT

In this study, the polyurethane based composites were prepared by solvent casting from dimethylformamid (DMF) solutions of Polyurethane-Polypyrrole (PU-PPy) in order to obtain the polyurethane based composites with enhanced dielectric properties for smart textile applications. From this research, it can be concluded that Glass Transition Temperature (Tg) values of the composites were influenced by the number of hydrogen bonds formed inside polyurethane in the presence of PPy. When the initial amount of pyrrole was increased, the Tg values of the composites were seen to increase. A correlation of the glass transition temperatures of the samples, determined by Differential Scanning Calorimeter (DSC) and Dynamic Mechanical Analyzer (DMA) via Young's modulus, showed that the increase of PPy reduced mobility and increased the glass transition temperature and modulus. Dielectric study results indicated that ~20% wt. Pyrrole (Py) increases dielectric constant above 7000 and these composites can be good candidates for electrical application.

Key Words: Polyurethane, Pyrrole, Glass transition, Young's modulus, FTIR-ATR.

ÖZET

Bu çalışmada, poliüretan-polipirol çözeltisinden dimetil formamid(DMF) çözücüsü kullanılarak tekstil uygulamaları için dielektrik özellikleri iyileştirilmiş poliüretan bazlı kompozitler elde edilmiştir. Bu çalışma ile polipirol varlığında kompozit malzemelerin camsı geçiş sıcaklığının (Tg), poliüretan içerisindeki hidrojen bağı miktarından etkilendiği sonucu çıkarılabilir. Pirolün başlangıç miktarı arttırıldığında, kompozit malzemelerin Tg değerlerinin arttığı görülmüştür. Diferansiyel Taramalı Kalorimetreden (DSC) elde edilen camsı geçiş sıcaklığı ve Dinamik Mekanik Analiz cihazından (DMA) elde edilen Young modülü sonuçlarının korelasyonu, polipirol arttıkça kompozitlerin hareket kabiliyetinin düştüğünü; camsı geçiş sıcaklığının ve modülünün arttığını göstermiştir. Dielektrik çalışmalarına göre, başlangıçta %20 Pirol içeren kompozit malzemenin dielektrik sabiti 7000' in üzerindedir ve bu malzemeler elektriksel uygulamalar için iyi birer adaydır.

Anahtar Kelimeler: Poliüretan, Pirol, Camsı geçiş, Young modülü, FTIR-ATR.

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1. INTRODUCTION

Polyurethanes (PU) are versatile materials used in a wide variety of application areas. Thermoplastic polyurethanes are well established in various applications because these materials combine the processability of thermoplastics with rubber like elastic properties. Some of the advantages of TPU are excellent tensile strength, anti- abrasion, wear resistance and flexibility at room temperature (1). Polyurethanes can be used in the textile industry, medicine, environmental fields and so on (2). Polyurethane has also been applied to waterproof-breathable fabrics, synthetic leather, antishrink wool, military textiles, adhesives and fine chemicals (3). Furthermore, combining ordinary fabrics with semi-conductive polyurethane films can lead to the development of smart textiles.

Conducting polymers are promising materials for specific applications and have attracted interest in recent years (4). Polypyrrole is a conducting polymer, which has been extensively studied due to its environmental stability and ease of synthesis. However, poor processability and mechanical properties limit its commercial applications. In order to overcome this problem, numerous methods have been studied (4, 5). The polymer-polymer composites, which contain conducting polymers, have been receiving attention due to their combination of good processability and mechanical properties with the electrical properties of conducting polymers (4). So, conductive polymers composites have been studied for their potential applications in electromagnetic interfacing, UV shielding, microwave absorption, sensors, electrical, optical, magnetic materials and devices (6).

Polyurethane properties depend on several factors and vary according to the selection of components and composition. Depending on these factors, this material can be cross-linked rigid, elastic foams or linear elastomers. Polyurethanes contain several polar groups, which enter into various interactions with each other, usually leading to phase separation and formation of soft and hard phases (7). Phase separated polyurethane structures are copolymers composed of a rubbery soft phase and crystalline hard phase. The hard segments are responsible for the dimensional stability and soft segments are responsible for the flexibility of the material. Hard segments provide physical cross-linking through hydrogen bonding and act as filler reinforcements to the soft segments (1). The properties of polyurethane elastomers reflect the balance of their structure. The extensional and low temperature properties of elastomers can be attributed to the soft segment. The interactions of soft and hard segments are also effective on the some properties of polyurethanes. The phase separation process restricts the formation of more integrated materials. If the compatibility of these materials were enhanced, the electrical properties would increase. Less phase separation leads to materials with enhanced mechanical and electrical properties (8, 9).

The aim of this study was to obtain and evaluate the electrical conductivity of the composites based on polyurethane and polypyrrole. The composites were prepared through casting, at 80 ^{0}C, after polymerizing pyrrole in matrix polymer. The composites were characterized by the Differential Scanning Calorimeter (DSC), the Dynamic Mechanical Analyzer (DMA), and the FTIR-ATR Spectroscopy. The electrical conductivity characteristics of the composites, prepared using different pyrrole fractions, indicate a high potential for their application in electrical processes.

2. MATERIALS AND METHODS

Thermoplastic polyurethane from Flokser Co. was used as a matrix polymer. It was the ester product of polyester polyol and diphenyl methane diisocyanate (MDI), the chain extender was 1, 4 butanediol. The molecular weight of the PU was determined by gel permeation chromatography. 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), acetonitrile (ACN, Aldrich, analytical), tetrahydrofuran (THF, Aldrich, analytical) were used.

In order to obtain polyurethane-based composites, pyrrole (Py) monomers were polymerized on polyurethane matrix. Figure 1 shows the preparation of composite films. Polyurethane (PU) was dissolved in DMF and Py with different initial weight ratios were added into the solution. After obtaining homogeneous solution, the initiator, Ce(IV) was added to the solution to polymerize pyrrole. After polymerizing pyrrole, excess solvent was evaporated by heat to obtain viscous polyurethane polypyrrole solutions. The viscous solutions were casted as films on 5×5 cm^2 glass substrate and dried at 80^{0}C for 24 hours in order to obtain dry samples without solvents. Drying conditions were determined according to previous studies (5). Generally, polyurethane films are dried under 60-80 ^oC and it takes at least 24 hours to evaporate DMF. For example, Bi and Pei prepared polyurethane films at 100 ^oC for 72h to evaporate excess DMF completely (10). The weight percentages of Py were calculated and reported using the initial weights of polyurethane, oxidant (20% of pyrrole) and pyrrole monomers (Py/(Py+PU+Ce(III)).

The characteristic functional groups of the samples and interactions were analyzed using a Fourier Transform Infrared Spectroscopy in the Attenuated Total Reflection Mode (Perkin Elmer FTIR-ATR Spectrum One with a universal ATR attachment with a diamond and ZnSe crystal). FTIR-ATR spectroscopy is also a convenient technique for the determination of the extent and strength of hydrogen bonding in organic molecules and polymers. TA Q800 Model Dynamic Mechanical Analyzer was used for analyzing mechanical properties of the composites. Young’s modulus was determined experimentally from the slope of a stress-strain curve created during tensile tests conducted on a sample of the composite material. The AC measurements were performed using Novocontrol Broadband Dielectric Spectrometer (Alpha-A High Performance Frequency Analyzer, frequency domain 0.001Hz to 3GHz). The samples were sandwiched between two gold electrodes with a diameter of 20 mm. Dielectric properties of composite thin films were evaluated on the basis of dielectric constant and its variation with frequency. The thermal analysis of the PU and the composites were performed by a Differential Scanning Calorimeter (TA instruments, USA) with a heating rate of 10^{0}C/min. The result of a DSC experiment, which was used to determine transition temperatures and enthalpies, was a curve of heat flux versus temperature.

3. RESULTS AND DISCUSSION

To determine whether PPy content influenced the mechanical properties, mechanical analysis was performed. Mechanical analysis shows that the composites showed an increase in Young's modulus as shown in Figure 2. Young's modulus, also known as the tensile modulus, is a measure of the stiffness of an isotropic elastic material. It is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke's Law holds. In general, hard segment content has an effect on the mechanical and thermo mechanical properties of PUs. The modulus has increased with hard segment content, which is due to the stiffness of polymer chain resulting from polymeric interactions. More hard segments led to the higher tensile modulus. As it can be seen from Figure 2, PPy in PU matrix has behaved like a hard segment and increased the values of Young’s modulus. The Young’s modulus values were 12,5 MPa and 20MPa for PU and PU-18%Py composites, respectively.

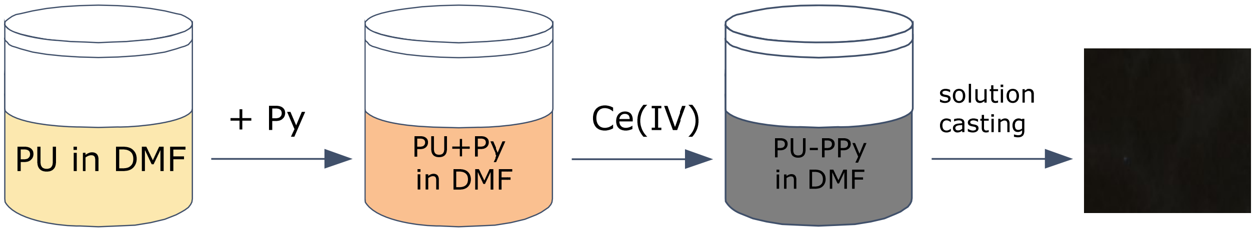

Figure 1. Schematic Illustration of the preparation of polyurethane-polypyrrole composite films

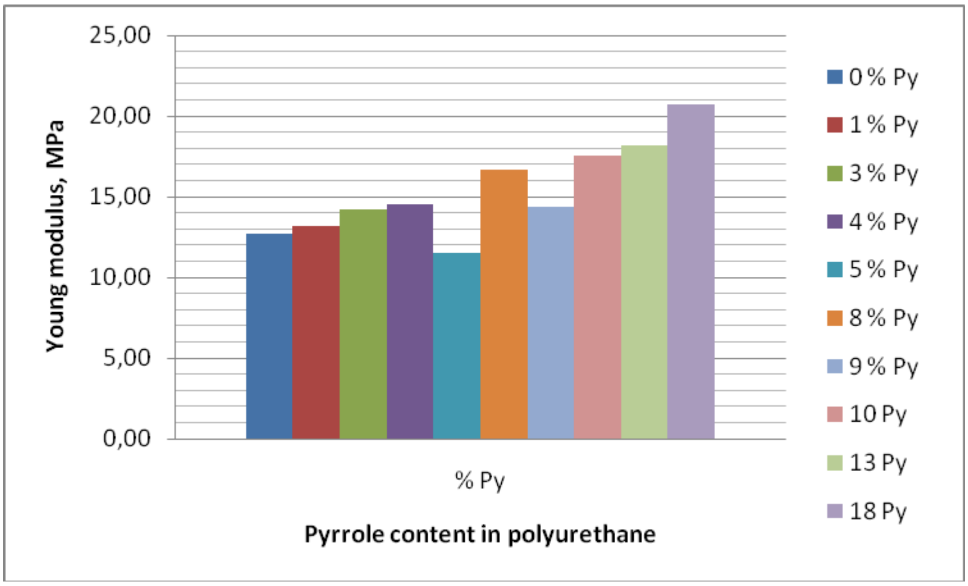

Figure 2. Young modulus values of the composites

The differential scanning calorimetry measurements were also carried out in order to establish the range of temperatures where thermal transitions occurred in the presence of PPy. The increased glass transition temperature, melting enthalpy, the onset point and temperature of melting as determined by DSC are shown in Table 1. The introduction of PPy into PU matrix has done little to disrupt the PU crystal structure in the case of 13% loading of pyrrole, however; at 26% pyrrole loading, the peak is sharper and intensity is deeper indicating a disruption in crystallinity due to an increase in the hard segment (Figure 3). Similar behavior has been previously reported for the polyurethanes with different soft segments and ascribed to hard segment interactions with the ester linkages (8). In our samples, melting temperatures were not affected considerably. However, melting enthalpy increased due to interactions and an increase in hard segment content with additional PPy.

For the segmented PU, it was noticed that the value of the melting temperature of the soft sequence did not vary according to the level of flexibility. This result was due not only to the reduction of the quantities of polyether, but also to the phase separation phenomenon. For the same reasons, the beginning of the melting phenomenon shifts towards lower temperatures as shown in Table 1. Moreover, a better organization of the hard sequence and the enhancements in Young's modulus values were noticed (Figure 2). This result is in agreement with those mentioned in the literature (11).

In addition to this, the introduction of PPy in PU matrix shifted the glass transition temperature of pure PU towards higher temperatures. According to literature (1), the glass transition temperature depends on the block lengths of soft segments and the quantity of hard segments. The observed results can be explained by strong interactions of polyurethane soft and hard segments, polypyrrole and oxidant. Furthermore, earlier work has demonstrated that in TPU, both the carbonyl and ether oxygens remain hydrogen bonded with the urethane NH groups (12). The H bonding interaction of NH groups of TPU with the carbonyl oxygen represents the extent of phase separation, and the same with ether oxygens represents the extent of phase mixing. Similar interaction of carbonyl and/or ether oxygens might be possible with the NH groups of PPy. The increase in Tg of the composites in the presence of PPy in PU matrix can also be related to phase mixing of soft and hard segments of PU. A possible explanation can be the interaction of NH hydrogens of PPy with the ethers' oxygens of the polyurethane.

Table 1. DSC results

Py (weight fraction)	Δh (J/g)	Tm (°C)	Tg (°C)	Onset point (°C)
0	3.7	37,49	-41,49	36,09
4	8.6	36,97	-38,28	36,15
5	3.9	35,46	-35.89	32,95
9	5.48	36.22	-38,51	33,07
13	4.9	37.53	-40,63	29,97
26	9.2	34.86	-20,96	32,65

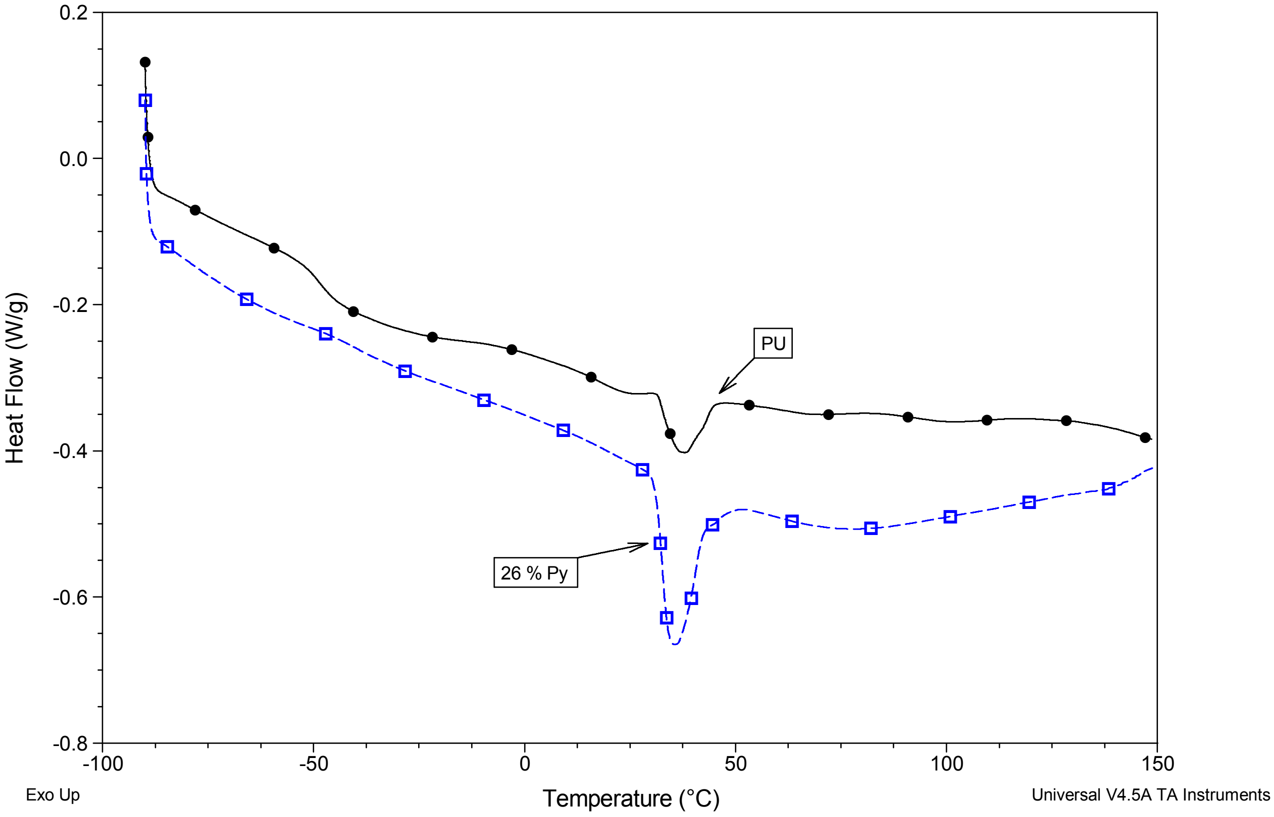

Figure 3. The differences in melting peaks of the samples.

The phase miscibility can be caused by the interactions through hydrogen bonding of NH urethane with the oxygen of the bridge ether present in the soft sequence (11). According to GPC results, the molecular weight of polyurethane is 135 640 g/mol. The molecular weight of the polyurethane-polypyrrole composite is 108 430 g/mol. The GPC result can be explained by a high grade of miscibility and phase mixing in the composite structures.

The characteristic functional groups of the samples were analyzed by using Fourier Transform Infrared Spectroscopy in the Attenuated Total Reflection Mode. Figure 4 shows a typical infrared spectrum of polyurethane. In lots of studies the bands centered at ~1730 cm^{-1} and ~1705 cm^{-1} are assigned to free and H-bonded carbonyl groups (13), respectively. The band at ~3340 cm^{-1} is typical for bonded NH groups (14). The bands at ~1040 cm^{-1} -1160 cm^{-1} are assigned for C-O esteric groups. CH_2 bending stretching appeared at 1390 cm^{-1}-1470 cm^{-1}.The bands at 2956 cm^{-1}, 1540 cm^{-1}, 1310 cm^{-1}, 1265 cm^{-1} are assigned to CH_2 stretching, CN stretching, CN bending, C=O stretching (13), respectively. The absorption band at 1066 cm^{-1} is also due to the ether C-O-C stretching.The incorporation of PPy and interactions between PU, PPy and oxidant was shown by FTIR-ATR investigation in Figure 5. The appearance of a new peak at 1640 cm^{-1} is associated with C=O and NH groups interactions. The increase in the absorbances of CH groups (at 1460-1310 cm^{-1}) with increasing the amount of PPy was observed (Figure 6). The vibrations at 1455 cm^{-1} (pyrrole ring), 1309 cm^{-1} (in plane=C-H) mark the presence of oxidized polypyrrole reported in earlier studies (15).

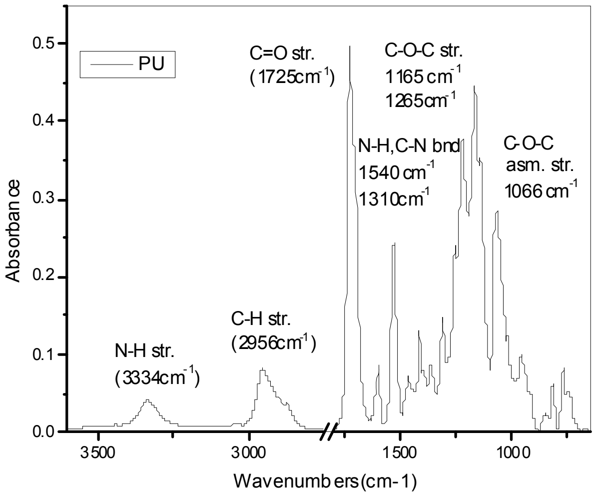

Figure 4. FTIR-ATR spectrum of polyurethane

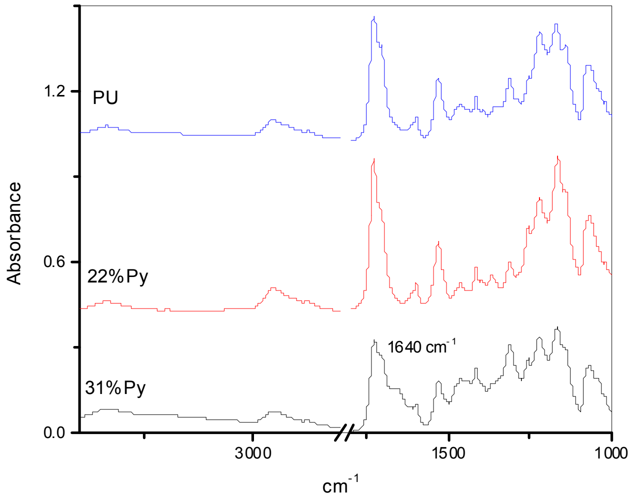

Figure 5. FTIR-ATR Spectrum of the composites

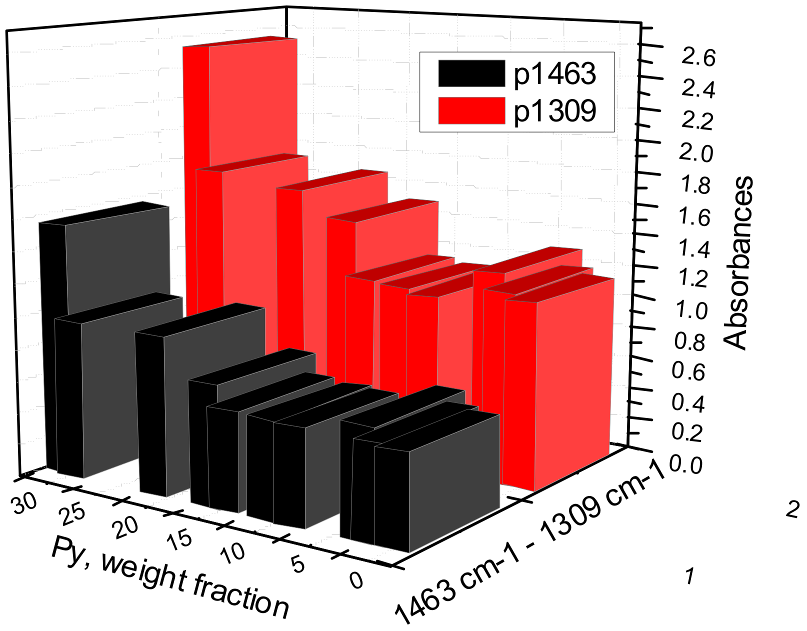

Figure 6. Increases in the absorbances versus pyrrole content

X-ray photoelectron spectroscopy (XPS) has been used to study the structure of conducting polymers. In particular, XPS has been used as a quantitative tool to predict the amount of conducting polymers incorporated in composites. N 1s spectra of polypyrrole contain amine (–NH–) and imine (–N=) components and can be identified by the peaks at binding energies of 398.2 and 399.6 eV (16). Figure 7 shows the XPS results of PU and PU/PPy composites. XPS results reveal that the component of nitrogen polaron sites (N1) increases with increasing PPy, which indicated that PPy chains have been incorporated into PU. It can be seen that the content of C1s decreased as PPy content increased.

The dielectric studies of composites versus frequencies and dielectric constants at 10^{-2} Hertz have been presented in Figure 8 and 9. Electrical conductivity measurements were carried out at room temperature (25 ◦C). These figures show that dielectric constants of the composites increase when the quantity of pyrrole is increased. The dielectric constant of $7x10^4$ was obtained in a composite containing 23% wt. of pyrrole.

In figure 7, we see that the dielectric constants of composites decrease with increasing frequencies. An explanation for this is that at low frequencies, the dipole movements and charge carriers can freely move within the material under test and follow the varying electromagnetic field, while at higher frequencies dipole and charge carriers become unable to follow variations of the applied electric field resulting in a decrease in the dielectric constant.

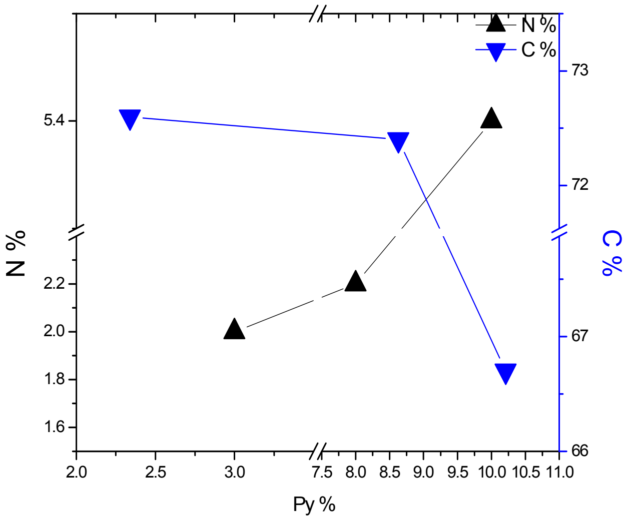

Figure 7. XPS spectra of PU and the composites

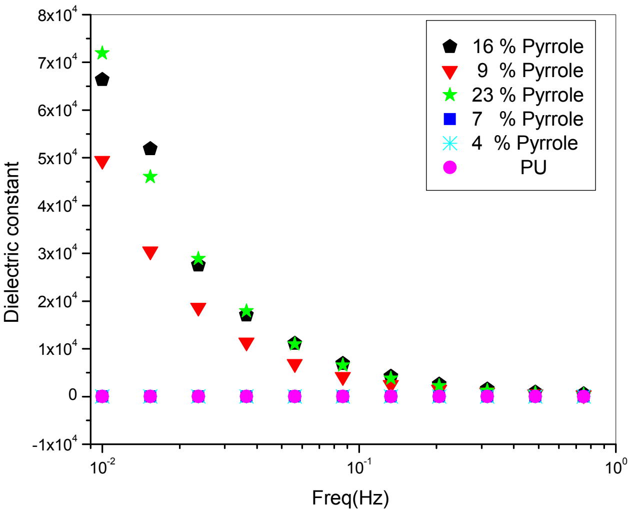

Figure 8. Dielectric constants of the composites versus frequencies

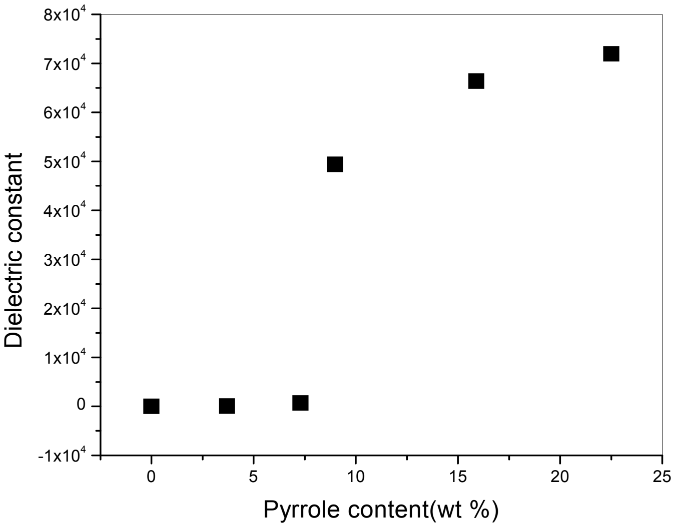

Figure 9. Dielectric constants of the samples at 10^{-2} Hertz.

4. CONCLUSION

Thermoplastic polyurethanes find use in a wide range of applications. In the current study, semi-conductive polyurethane-based composites were prepared successfully with the aim of opening the way to new applications in the fields of energy storage, microelectronics, textiles, sensors, electroluminescence and electromagnetic interference (EMI) shielding. Pyrrole monomers were polymerized on polyurethane matrix to obtain polyurethane-polypyrrole composites.

DSC, DMA, FTIR ATR and dielectric spectrometer were used to obtain characteristics of the composites such as molecular chain mobility, glass transition temperatures, thermal transitions temperatures, and modulus, mechanical and dielectrical properties. A variation of the polypyrrole amount led to an increase in the Tg values. The Tg values of polyurethane was -41^{0}C, while Tg values of the composite with 20% Py was -21^{0}C as determined by DSC. The increase in glass transition temperature of polyurethane after the introduction of PPy in PU matrix revealed the interaction of polyurethane soft and hard segments, pyrrole and oxidant.

Furthermore, approximately 60% increase in Young's modulus was determined by DMA. As a result of thermal and mechanical studies, a better organization of the hard sequence and the enhancements in Young's modulus values were noticed. The mechanical and thermal behavior of the material supported the complex interactions.

The spectral analysis indicated that interactions between carbonyl groups of urethanes and NH groups of PPy strongly intensify when PPy content exceeds ~20%. A new peak at 1640 cm^{-1} was observed as a result of pyrrole polymerization in polyurethane matrix. The appearance of a new peak at 1640 cm^{-1} was associated with C=O and NH groups interactions.

XPS analysis has been used as a quantitative tool to determine the incorporation of conducting polymers in composites and the results indicated that PPy chains have been incorporated into polyurethane.

Electrical conductivity measurements show that dielectric constants of the composites increase with increasing pyrrole content and decrease with increasing frequencies. Approximately 20% wt. pyrrole increased dielectric constant above 7000. Consequently, dielectric study results showed that the composites can be good candidates for electrical application.

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