International Journal of Nanoelectronics and Materials
Volume 12, No. 4, Oct 2019 [423-436]

Preparation and Characterization of Electrical, Morphological and Topographic Properties for Advanced Conductive PMMA/PVDF/PANI Ternary Blend for Low Percolation Threshold Devices

Asra Ali Hussein[1*]

[1]*Babylon University /Collage of Material Engineering /Polymer and Petrochemical Industries/Iraq.*

Received 1 November 2018, Revised 5 March 2019, Accepted 9 April 2019

ABSTRACT

The presented work targets on developing an advanced conductive polymer blend. This polymer has a low permeation threshold at low concentrations of conductive polymer. Two groups of polymer blend, consist of a mixture of polyvinylidene fluoride (PVDF), polymethyl methacrylate(PMMA) and polyanylene (PAni) were used. The first group was used with various weight fractions (1%, 3% and 5%) of Pani, while second group (10%, 30%, and 50%) of PVDF was used via solution casting method. The tests carried out were the AFM, FTIR, SEM as well as analysis of electrical conductivity. The results show that the dielectric constant was observed to saturate at mid frequency of 10^3*Hz –* 10^5 *Hz. At low frequency (*10^1 *Hz), Cp, dielectric constant and impedance resistance were high. Moreover, it could be observed that the Cp, dielectric constant and impedance resistance value for optimized samples was decreased for group PMMA-30%PVDF-5%PAni more than PMMA-50%PVDF-5%PAni. The AFM results demonstrate the topographic of neat PMMA where bigger globules can be seen. Little amounts of these globules were noticed in the ternary blend of PMMA-PVDF– PAni. AFM micrograph of ternary blend demonstrates that the expansion of PVDF wt.% in the blend reduces straightened globules. In the second group, the ternary blends were smoother than neat PMMA. The FTIR investigation demonstrates the higher absorptivity peak because of C - O aggregate shows up in the ternary blend. A slight move of the crest at 1727 from 1730* cm^{-1} *for neat PMMA might be owing to the good homogeneity of PMMA matrix with PAni and PVDF in the ternary blend. Morphological properties represented by SEM image illustrates homogenous mixing for both groups. In PMMA-50%PVDF-5%PAni blend, the zone involved by PAni has been restricted which results in a lower permeation threshold of PAni, and an expansion in the conductivity of the sample as compared with counterpart group PMMA-30%PVDF-5%PAni.*

Keywords: Ternary Blend, PAni, Percolation Threshold.

1. INTRODUCTION

Since the disclosure of characteristically conducting polymers around three decades back, this particular type of polymers has received much consideration because of its unrivaled properties. Among the mentioned polymers, polyaniline (PAni) is the most examined leading polymers because of its controllable and moderately abnormal state of electrical conductivity combined with great stability to environment conditions, electrical and optical properties, consumption opposition, ease crude materials and simplicity of union in significant returns [1]. Subsequently, it offers scope for an assortment of potential mechanical applications, for example, in static membrane for diaphanous packaging of electronic segments, electromagnetic

---

[*] E-mail: *asra.ali96@yahoo.com*

protecting, battery-powered batteries, actuators, optical sensors and even layers for partition of gas mixtures [2].

However, because of poor processability and weak mechanical properties of PAni, it has been mixed with various thermoplastic polymers including polyethylene, poly (methyl methacrylate) (PMMA) and with poly (vinylidene fluoride) (PVDF). Additionally, PVDF is fascinating because of some exceptional properties of PVDF, in particular, astounding mechanical properties, synthetic and weathering opposition, piezo-electric properties and great adaptability [3].

Researchers have used the methodology of examining the binary and ternary blend, which consist of conductive (PAni) and piezoelectric PVDF and PMMA. This methodology is utilized to accomplish the objective of this exploration, which is to assemble an establishment of strategies to diminish the permeation threshold of parts in multi-segment blends [1,4,5]. This research targets on developing advanced morphologies to produce highly conductive materials where PMMA, PVDF and Pani are blended into two groups. Morphology, topography and electrical properties were characterized.

2. MATERIALS AND METHODS

Polyvinylidene fluoride, (PVDF) was selected for this work with a density (1.78 g/cm^3) and particle size of (16μm). This material was supplied by China Guangzohou Li Chang Floro plastics Co., Ltd and was characterized by DSC and FTIR tests. PMMA with a density (1.18g/cm^3) and particle size of (14.59 μm) was supplied by Sigma Aldrich Inc. Korea. PANI-W100 water dispersed with particle size about 25 nm and diameter of 20 nm was supplied by Panichem Co. Ltd. Korea. DMF was supplied by central drug house CDH (P) Ltd. India.

3. PREPARATION PROCEDURE

Two group of ternary blends were synthesized (six blends). PMMA was adopted as a base material of the mixtures. The preparation of first group included pure sample solution, binary polymer blends and ternary blends with various concentration of PAni (1%, 3% and 5%). The optimized sample was used to prepare the second group with variety concentration of PVDF (10 wt.%, 30 wt.% and ,50 wt.%). In the first group, all samples were prepared using a blend of (50wt.%PMMA+50wt.%PVDF) dissolved in DMF on stirrer using magnetic stirrer for four hours with 70°C to get homogenized solution. PAni dispersed in DMF was using ultra sonication for about 15 minutes. Then, PAni Solution was added drop by drop to the blends, thereafter mixing on stirrer without heat for about 3 hours to get homogenous solution. The second group was prepared by mixing PMMA with various wt. % PVD and fixed amount of PAni (5wt.%). The homogenous solution was casted in Petri dish of a suitable size. The samples were left in air atmosphere to dry and remove all the solvent.

4. EXPERIMENTAL STUDIES

D.C electrical studies were analyzed using a casted film by the vertical thickness of the substrate atmosphere temperatures. The analysis was done using a Keithley electrometer type 6517. The specimen was set between two samples holders and a DC voltage was connected utilizing two-point test gear. The experiment was conducted under a voltage range of 0-1000V and an ammeter range of 0-20mA. Five measurements of conductivity were taken for each sample and the readings were averaged to represent this sample.

The microstructural analysis was carried out utilizing SEM (LEO, model 1455VP, UK), with an accelerating voltage of 10–20 kV to diagnose the phases morphology of the ternary blend. AFM technique was used to study the surface roughness and topography of the prepared samples. Anon contact mode was utilized to scan various locations on the films at various scan size using scanning probe microscope type (BY300). These scans were repeated for the two groups of ternary blends. Structural properties and the formation of new bond were studied using FTIR analyzer type (IRAFFINITY-1) (Shimatzu) from the range (500-4000) of wave length.

5. ELECTRICAL STUDIES

Impedance value, C_p, and dielectric Constant for two groups of polymer blend were calculated for the first group with different weight fraction of PAni, as shown in Table 1. The second group with different weight fraction of PVDF is shown in Table 2 while variation of C_p at various frequencies was shown in Figure 1 to Figure 12. Three categories of frequencies in this test were used namely low, medium and high frequency which range between 10^1Hz - 10^3 Hz, 10^3Hz – 10^5 Hz and 10^5Hz - 10^6 Hz respectively. It can be noticed from the figures that Cp , dielectric constant and impedance resistance at low frequency region (10^1 Hz to 1 kHz), increased with frequency for both groups and for optimized samples PMMA-50%PVDF-5%PAni and PMMA-30%PVDF-5%PAni. The dielectric constant was observed to saturate at medium frequency (10^3 Hz – 10^5 Hz), before diminishing progressively at high range of frequency 10^5 Hz - 10^6 Hz. At a low range (10^1 Hz), the PVDF chain structure, undergo orientation polarization, which leads to permanent dipole moment in the polymer structure. Consequently, Cp, dielectric constant and impedance resistance detected were in the same low range with frequency but increases with increasing PVDF as shown in Figure 2, Figure 5 and Figure 8 respectively [6]. Moreover, after chosen the optimized samples from both groups, it could be observed that the Cp, dielectric constant and impedance resistance values were decreased faster for group PMMA-30%PVDF-5%PAni than PMMA-50%PVDF-5%PAni, as revealed in Figure 3, Figure 6 and Figure 9 respectively. The reduction in values of Cp, dielectric constant and impedance resistance is due to increase concentration of PVDF in PMMA-50%PVDF-5%PAni and PVDF, which has extraordinary potential in insulating and increasing dielectric constant. This is because, high dielectric constant consequently increases Cp [7]. Moreover, the relationship between capacitance and dielectric constant is positive where Cp increases with the increasing dielectric constant. As shown in Figure 1 and 2, Cp and dielectric constant of PMMA-50%PVDF-5%PAni are higher than PMMA-30%PVDF-5%PAni.

Figure 10, Figure 11 and Figure 12 represent electrical conductivity variation with frequency for both groups and for selected samples. The PMMA-30%PVDF-5%PAni and PMMA-50%PVDF-5%PAni show electrical conductivity increases with increasing frequency. The samples show percolation thresholds at small concentration of PAni (1 wt.% to 5 wt.%) which agrees with a previous study [7]. Moreover, the conductivity of PMMA-30%PVDF-5%PAni is higher than PMMA-50%PVDF-5%PAni. This is due to the increasing of weight fraction of PVDF in PMMA-50%PVDF-5%PAni, which agrees with a previous research [8].

Table1 First groups of samples

PMMA wt.%	PVDF wt.%	PAni wt.%
50	50	1
50	50	3
50	50	5

Table 2 Second group of samples

PMMA wt.%	**PVDF wt.%**	**PAni wt.%**
90	10	5
70	30	5
50	50	5

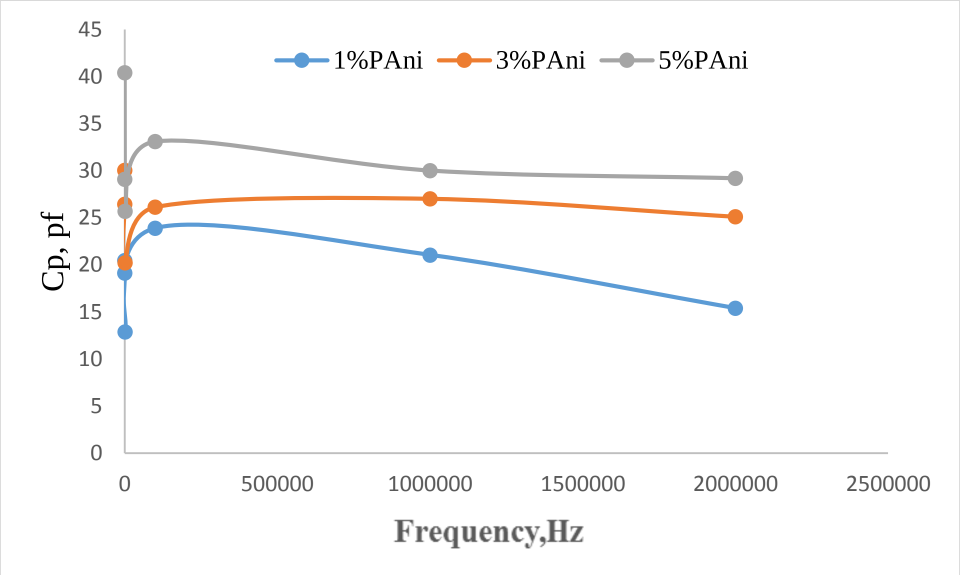


Figure 1. Variation of Cp with Frequency for various wt. % of PAni.

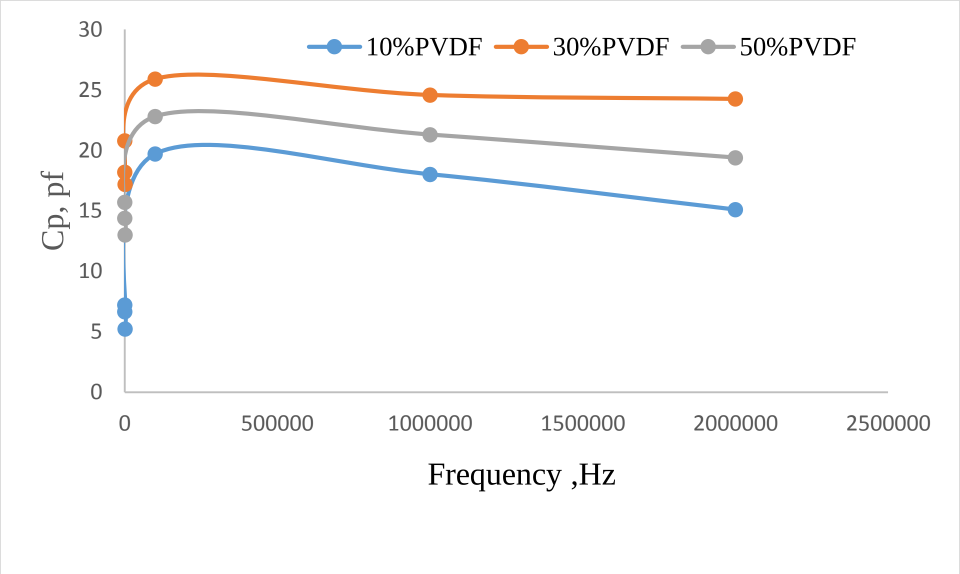


Figure 2. Variation of Cp with Frequency for various wt. % of PVDF.

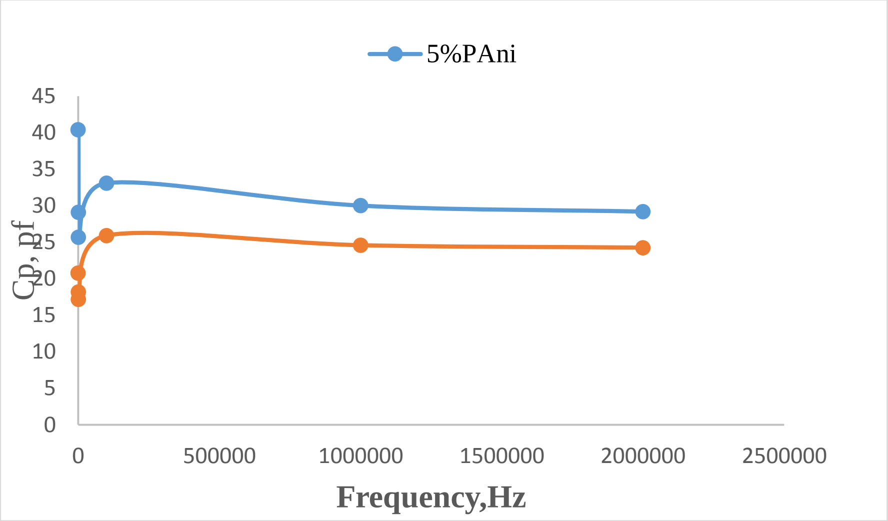


Figure 3. Variation of Cp with Frequency for optimized specimens.

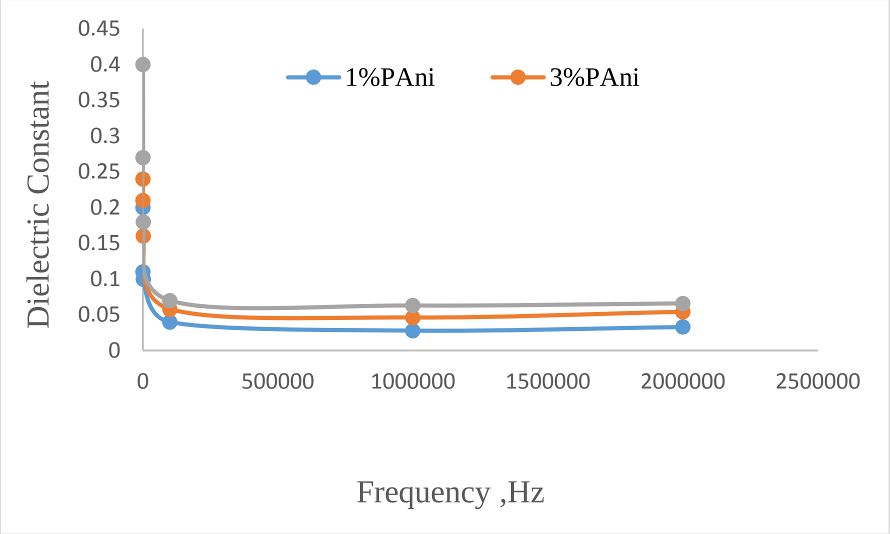


Figure 4. Variation of dielectric constant with Frequency for various wt. % of PAni.

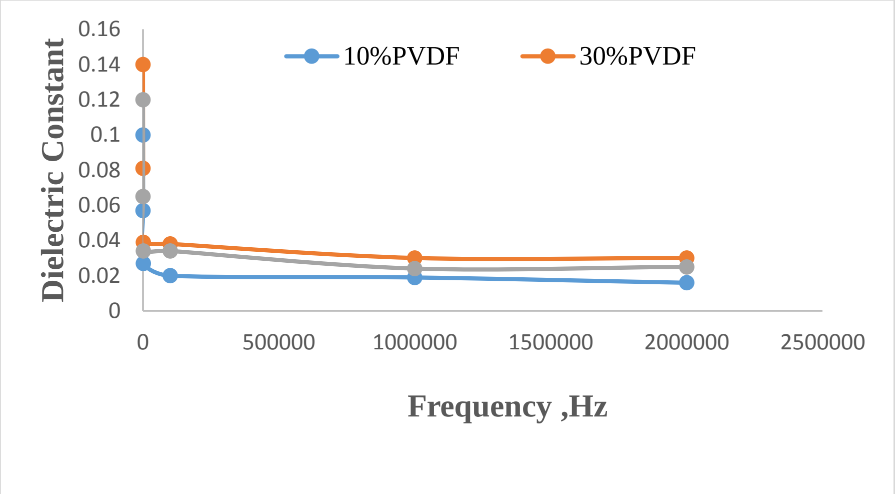


Figure 5. Variation of dielectric constant with Frequency for various wt. % of PVDF.

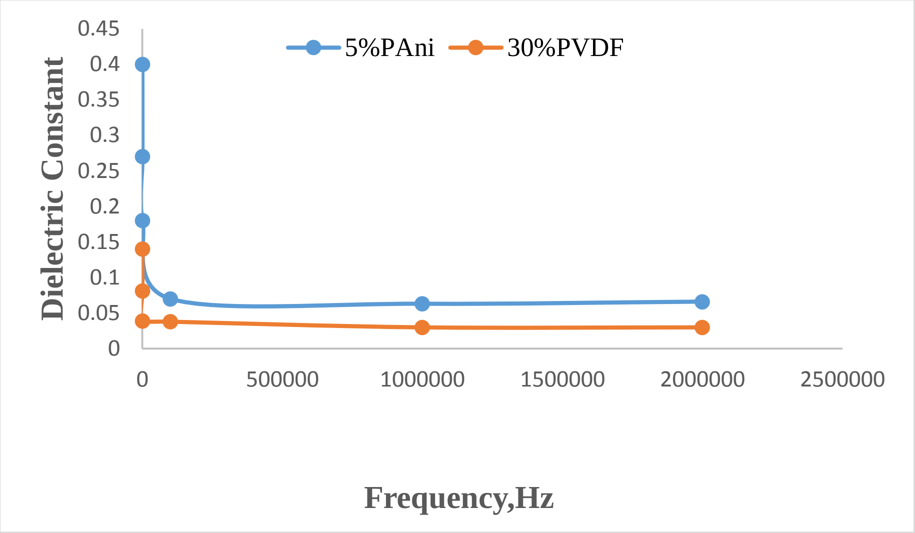


Figure 6. Variation of dielectric constant with Frequency for optimized specimen.

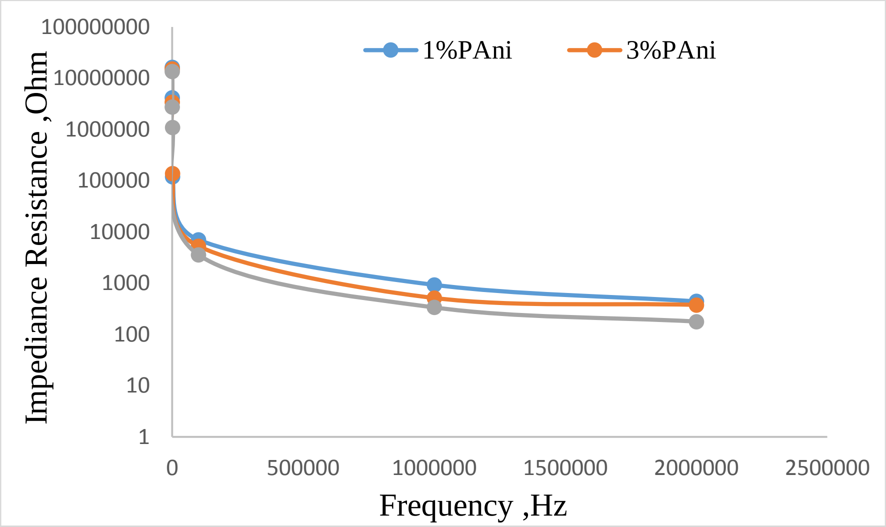


Figure 7. Variation of Impedance resistance with Frequency for various wt. % of PAni.

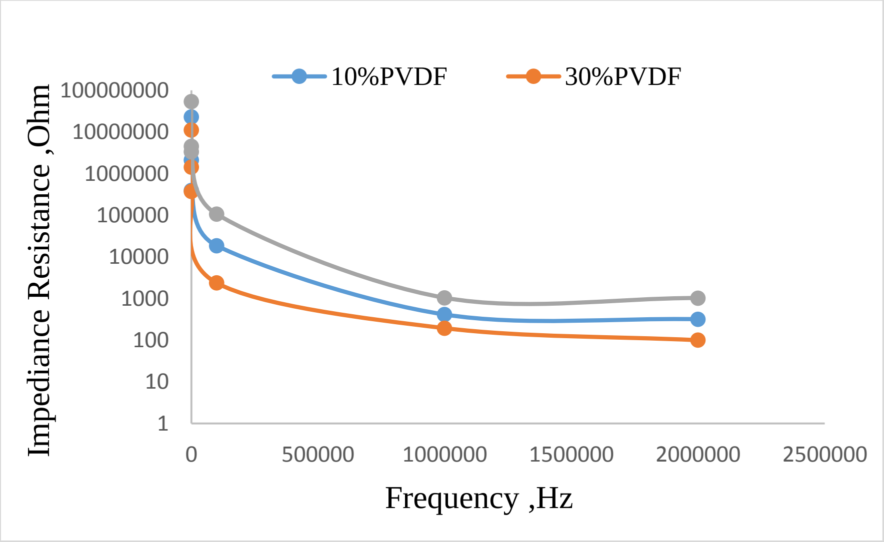


Figure 8. Variation of Impedance resistance with Frequency for various wt.% of PVDF.

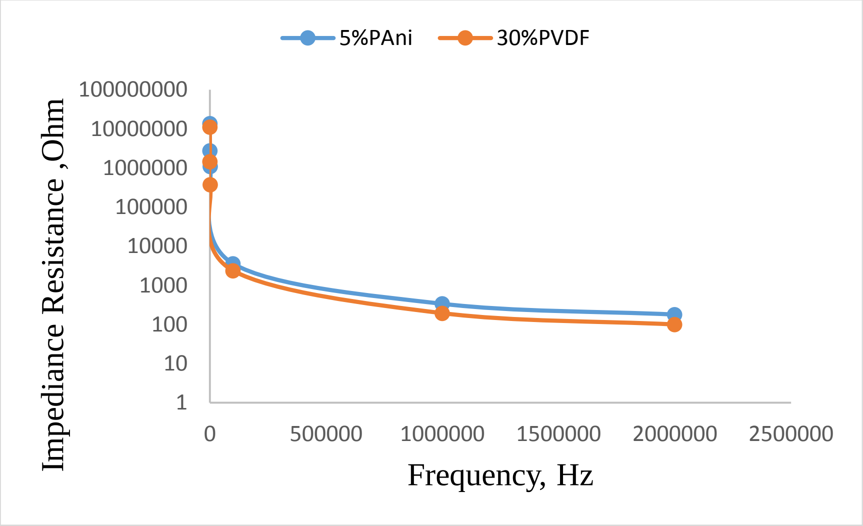


Figure 9. Variation of Impedance resistance with frequency for optimized specimens.

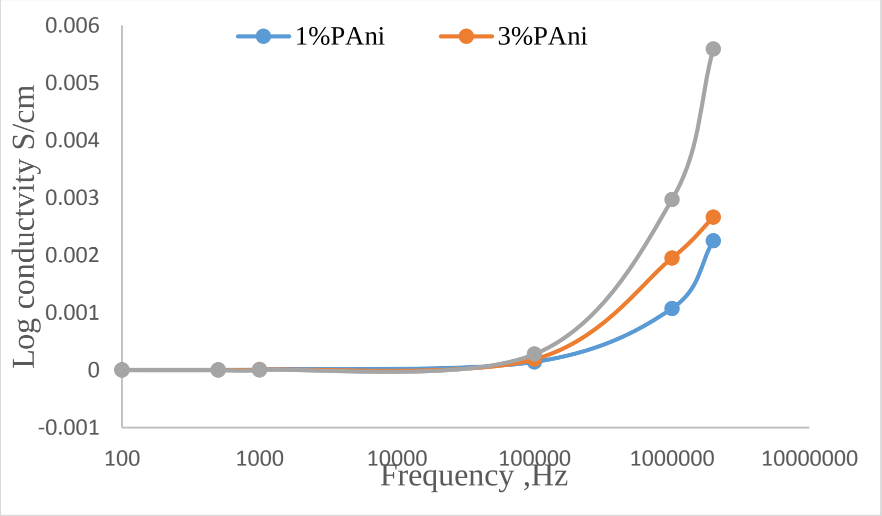


Figure 10. Electrical conductivity as a function of frequency for various wt.% of PAni.

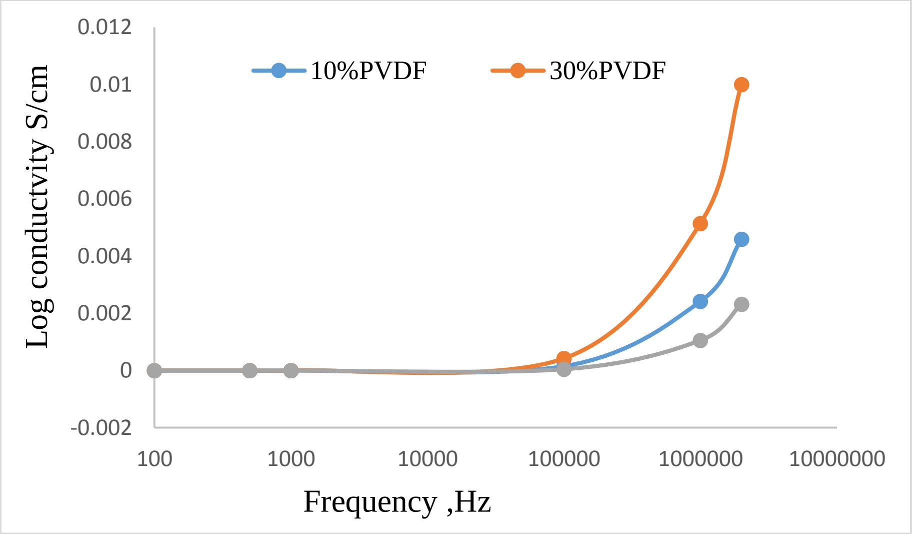


Figure 11. Electrical conductivity as a function of frequency for various wt.% of PVDF.

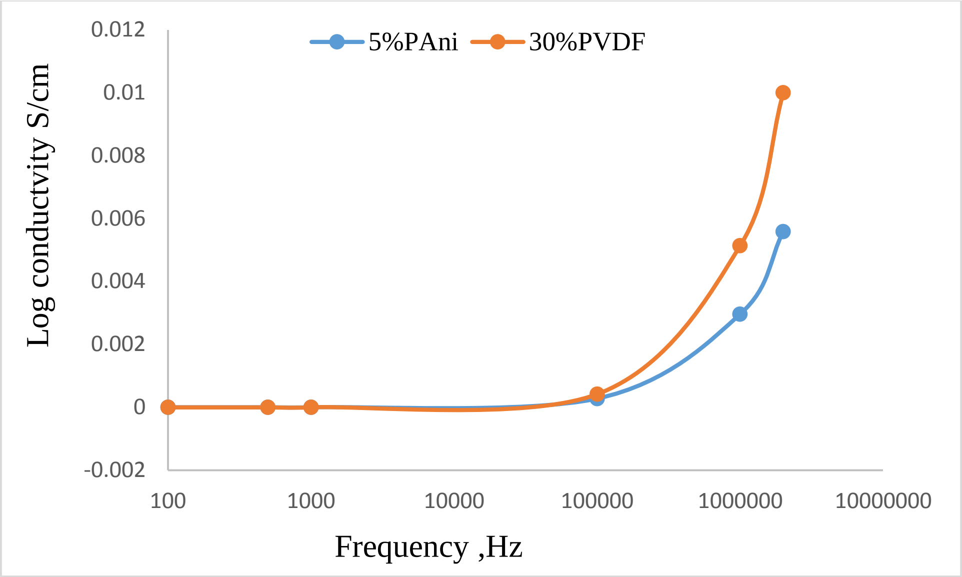


Figure 12. Electrical conductivity as a function of frequency for optimized specimens.

6. FTIR STUDIES

FTIR analysis was utilized to demonstrate the structural analysis of pure PMMA and ternary blends of PMMA/PVDF/PAni as revealed in Figure 13. The assessment was in the scope of 4200–500cm^{-1}. The absorption spectra of PANI for the prepared samples at 14010cm^{-1} corresponds to extending of CH_2, while the medium bands at 1309 and 1226 cm^{-1}refer to the extending C –N, the peaks at low wave number 889 and 801 cm^{-1} and at 578 and 495 cm^{-1} is for bending of C -H and C- C [9]. For PVDF, the observed band at 1426cm^{-1} corresponds to bending and swaying of CH_2. The vibrational band at 1406 cm^{-1} is due to stretching of the antisymmetric C –C bond and at 1383cm^{-1} is due to stretching of asymmetric CF_2, while at 1214 cm^{-1} is referred to wagging of CH_2. The vibration modes due to stretching symmetric CH_2 and twisting of CH_2 appear at 1184cm^{-1}. The peak at 1152 cm^{-1} is assigned to rocking of CF_2 and stretching of asymmetric C–C. The low vibration at 873 cm^{-1}and 492 cm^{-1} are assigned to stretching of symmetric C–C, bending of CF, CH, and CF as well as wagging and bending of CF_2 [9]. The characteristic band for the neat PMMA is illustrated at 1449 cm^{-1} for twisting of OCH3. The one at 1487cm^{-1} refers to scissoring of CH_2 while 1066 cm^{-1} corresponds to extending of symmetric C-C [10]. The higher vibration bands in the ternary blend are due to C -O group. The little movement of peaks 1728 cm^{-1} from 1731 cm^{-1} for neat PMMA could be assigned to homogenous blending between the PMMA, PVDF and PAni. The significance of testing is to confirm the expected functional groups which reveals the structure of the prepared ternary blend in group 1 and group 2. Moreover, the functional groups have the great effect on enhancing electrical and thermal conductivity of polymer composites. The results show no change in chemical structure [11]

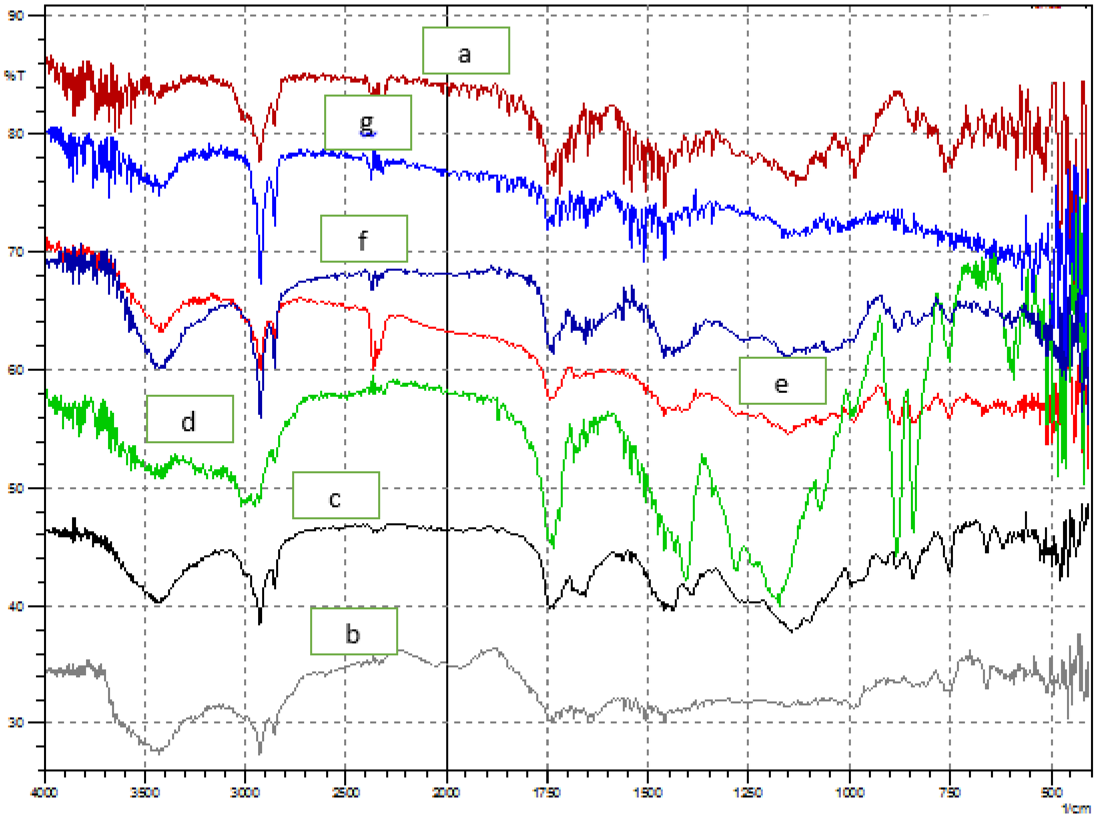


Figure13. FTIR Spectrum of ternary blend group 1and group 2 as a function of wavelength.
a. Pure PMMA b.10%PVDF c.30%PVDF d.50%PVDF e.1%PANI f. 3%PANI g.5%PANI.

7. ATOMIC FORCE MICROSCOPY (AFM) ANALYSIS:

The specimens were examined with AFM method by utilizing non-contact modes. The AFM scanning was accomplished on different areas on the films and was done at various scanning sizes. All prepared films PMMA, and PMMA-PVDF– PAni, were scanned at one side.

The values of root mean square (RMS) roughness were achieved, as included in Table 3. The measurement of roughness was carried out with the same size. Apparently, from the topographic image of PMMA as Figure 14, the globules appear bigger but in smaller amounts than in the ternary blends PMMA-PVDF– PAni. AFM images of ternary blend (Figures 14 and 15) demonstrated that the expansion of PVDF or PAni wt.% in the blends gives a lessening in the smoothed globules. This can be best seen in Figure 14c, Figure 14d, Figure 15b and Figure 15c. The quantity and type of reinforcement used certainly will affect the quantity of smoothened globules in the prepared samples [12].

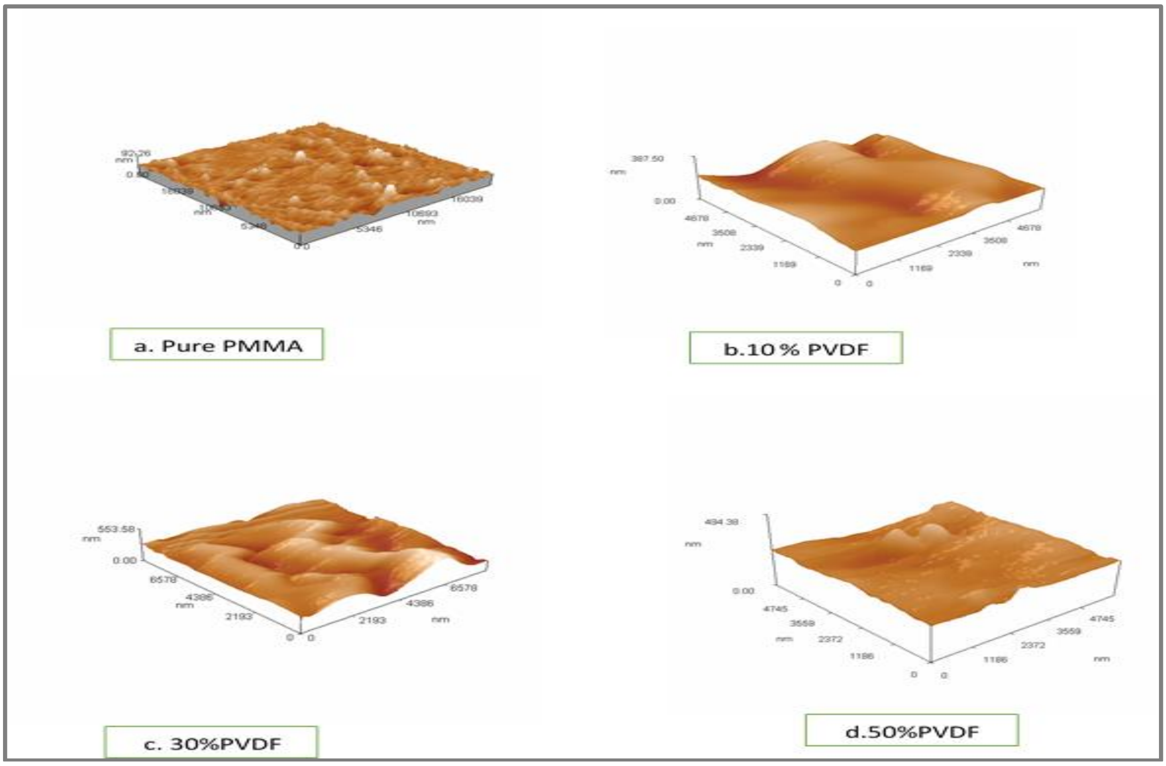
Table 3 AFM data for surface roughness of group 1 and group 2 of ternary blends

Percentage	**Root mean square Sq (group 1)**	**Root mean square Sq (group2)**
Pure PMMA	64 nm	
1%PAni	30.9 nm	
3%PAni	25.7 nm	
5%PAni	21.7 nm	

10%PVDF		31.8 nm
30% PVDF		46.5 nm
50% PVDF		22.7 nm

AFM images of the second group show the same behavior as shown in Figure 15. It is clear that ternary blends are smoother than pure PMMA. Figure 14 and Figure 15 reveal the homogenous mixing of the three polymers with different concentration.

Generally, the image of topography and the calculated value of roughness show that the PAni plays major role in changing the topography of samples surface. The samples surface has been altered by adding PAni, which results in development of the PAni accumulation in the fissure or pits of PMMA and PVDF. Besides, these lines smoothing out the specimens surface and lessening the roughness, as presented in Table 3. It is clear that changing the PAni concentration affect the surface roughness of the first group samples. The presence of this different phase of PAni does not reject the PAni arrangement in a thin subsurface layer of the PMMA matrix [13].



a. Pure PMMA

b.10 % PVDF

c. 30%PVDF

d.50%PVDF

Figure 14. AFM image for group 1 of pure and ternary blends.

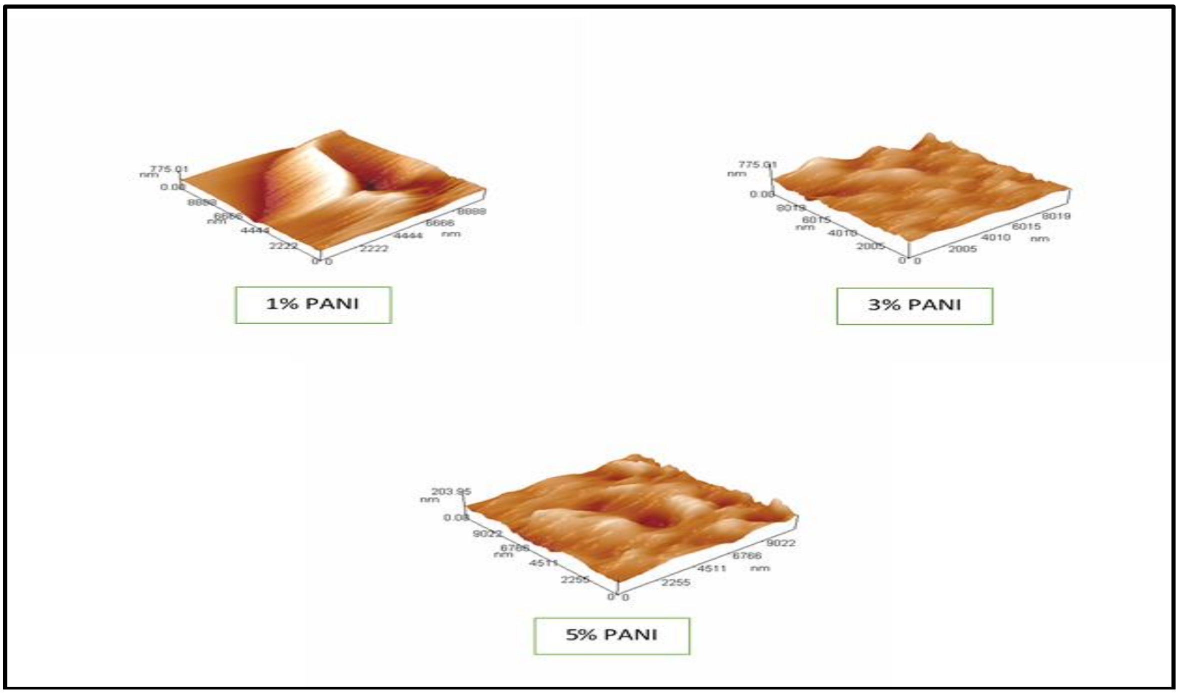


Figure 15. AFM image for seconed group of ternary blends.

8. MICROSTRUCTURAL ANALYSIS (SEM)

The morphology of prepared ternary blend is represented by a sample from the first group which is (PMMA-30%PVDF-5%PAni) and a sample from the second group (PMMA-50%PVDF-5%PAni). These samples were examined using SEM technique. Figure 16 and Figure 17 distinctly affirms that in a triple-permeated structure with PAni as the internal phase, PAni will disperse. As shown in Figure 16, the PAni network in a multi-permeated structure has branches with thin dividers. As per the positive spreading coefficient of PVDF over PAni, PVDF is compelled to the interface. For this situation, PAni and PMMA arranged in within and outside while PVDF situates at the interface. This is because of the lower interfacial tension among PVDF and PAni, the interfacial adhesion of the whole PAni and PVDF in one another, and the development of little phase sizes. Besides, when the concentration of PMMA is higher, the PAni arrangement is better and uniform with homogeneous branches circulated all through the sample. Figure 17 shows the PMMA-50%PVDF-5%PAni ternary blend, a blend of both crystalline phase of PVDF spherulites and amorphous structure of PMMA containing highly distributed PAni. This may explain the higher conductivity acquired for 50%PVDF/50%PMMA blend containing 5 wt.% of PAni when contrasted with the blend containing PMMA-30%PVDF-5%PAni [9].

Nevertheless, by diminishing the weight fraction of PVDF to as meager as 30% (as shown in Figure 16), the quantity of huge PVDF islands reduces. These vanishings of huge PVDF parts leads to the decrease of the concentration of PVDF until no large PVDF parts can be seen. Nonetheless, the extensive parts of PVDF assume a vital role in decreasing the permeation threshold of PAni, as they possess a few spaces in the blend and utmost the nearness of PAni in those zones. It is presumed that this is a standout amongst other methods for decreasing the permeation threshold, in spite of double percolated structure. In a PMMA-50%PVDF-5%PAni blend, the zone involved by PAni has been restricted. In Figure 17c and Figure 17d, it can be seen that persistent phase of PVDF and PMMA, and substantial PVDF zones when contrasted with the counterpart group. These lead to lower permeation threshold of PAni, and an expansion in the conductivity of the sample [14, 15], as revealed by impedance resistance of the samples in Figure 3.

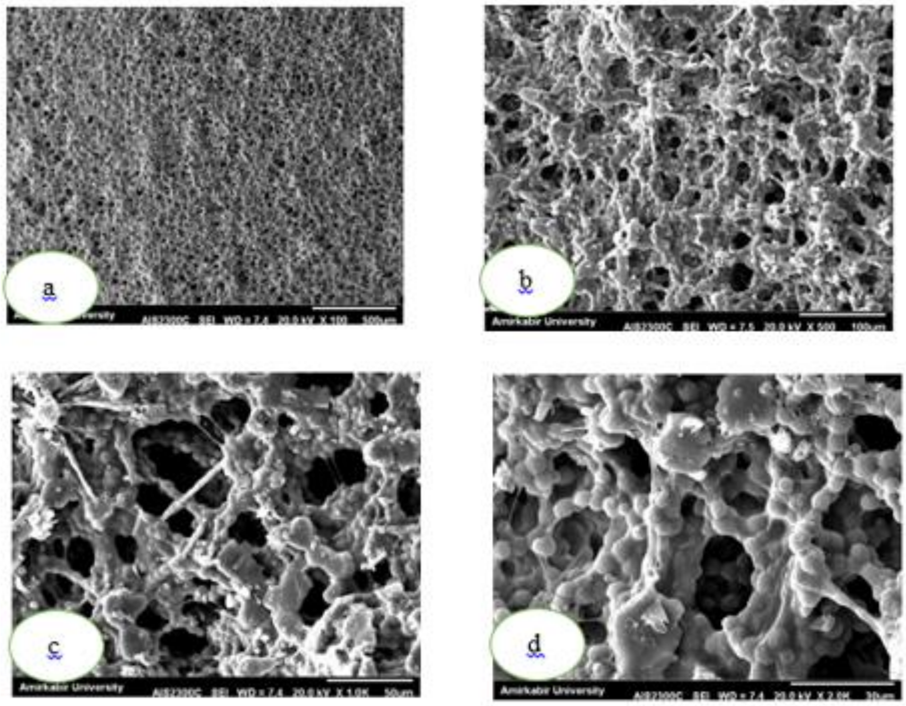


Figure 16. SEM image of fractured surface of samples as a function of PVDF wt. %, PMMA-30%PVDF-5%PAni.

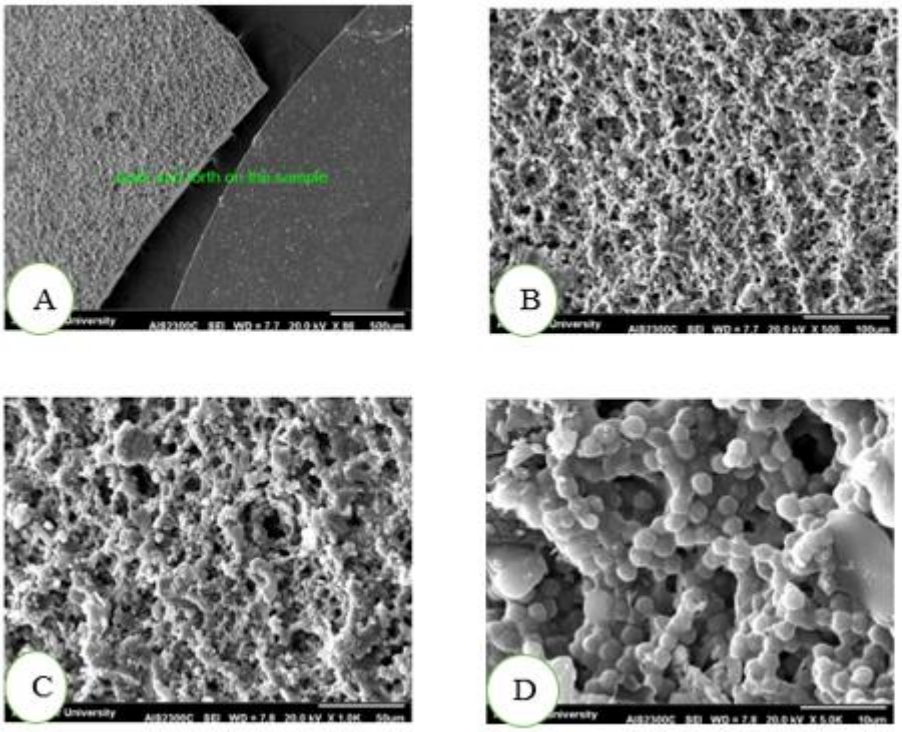


Figure 17. SEM image of fractured surface of samples as a function of PVDF wt. PMMA-50%PVDF-5%PANI.

9. CONCLUSION

The objective of this work is to develop multi-component phase morphology of blends. This morphology was performed by fabricating two groups of PMMA/PVDF/PAni ternary blends using solution-mixing method. This study aims to evaluate the triple-percolated morphology to decrease the percolation threshold of all phases in the prepared blend. The results showed that dielectric constant is saturated at mid frequency (10^3 Hz – 10^5 Hz). At a low frequency (10^1 Hz), Cp , dielectric constant and impedance resistance were high. AFM topographic of neat PMMA shows an increasing in globules size but still smaller than in the ternary blends PMMA-PVDF–PAni. AFM images of ternary blends showed that the increase of PVDF or PAni Concentration in the blends contributes to a decrease in smoothened globules. In the second group, the ternary blends are smoother than the neat PMMA. The entire arrangement of the outcomes shows relationship between the structure and the electrical properties of PMMA– PVDF– PAni ternary blends. The SEM images illustrated homogenous mixing for both groups. In the PMMA-50% PVDF-5%PAni blend, the zone involved by PANI has been restricted which results in a lower permeation threshold of PAni, and an expansion in the conductivity of the sample as compared with the counterpart group (PMMA-30%PVDF-5%PAni).

REFERENCES

[1] Fratoddi, Venditti, Cametti, Russo M. V., 2015. Sensor Actuator B Chem **220** (2015) 534-548.
[2] Luiz F. Malmonge, Giovana de A. Lopes, Simone do C. Langiano,José A. Malmonge, Joo M. M. Cordeiro, Luiz Henrique C. Mattoso, European Polymer Journal. **42** (2006) 3108–3113.
[3] A. K. Tomar , Suman Mahendia, Rishi Pal Chahal and Shyam Kumar, AIP Conf. Proc. 1393 (2011) 145.
[4] Ravati Sepehr, thesis submitted to university of De Montreal, (2010).
[5] Ievgen Duboriz and Alexander Pud, Sensors and Actuators B: Chemical. **190** (2014) 398–407.
[6] M.D. Rozana, A. N. Arshad, M. H. Wahid, M. N. Sarip & M. Rusop, International Journal of Research in Science (ISSN Online: 2412-4389) IJRS **3** ,1 (2017).
[7] Malmonge LF, Mattoso LHC., Polymer. **36** (1995) 245–9.
[8] Shiyong Yang & Eli Ruckenstein, Synthetic Metals. **59** (1993) 1-12.
[9] Sudip Ray, Allan J. Easteal, Ralph P. Cooney, Neil R. Edmonds, Materials Chemistry and Physics. **113** (2009) 829–838.
[10] Jin-Woo Park,Yun-Ah Seo,Il Kim, and, Chang-Sik Ha, Keitaro Aimi and, and Shinji Ando, Macromolecules. **37**, 2 (2004) 429-436
[11] Supri A. Ghani & Heah Chong Young, Journal of Physical Science **21**, 2 (2010) 81–97
[12] Nizamara S. Pereira, Maria J. A. Sales, Artemis M. Ceschin, Polímeros. **22**, 4 (2012) 384-389.
[13] V.N. Bliznyuk, A. Baig, S. Singamaneni, A. A. Pud, K. Yu. Fatyeyeva, G. S. Shapoval, Polymer, xx (2005) 1–9.
[14] Zilberman, M., Siegmann, A., & Narkis, M., Journal of Macromolecular Science – Physics. B**39**,3 (2000) 333-347.
[15] Yuan, Z. & Favis, B. D., Journal of Polymer Science, Part B: Polymer Physics. **44**, 4 (2006) 711-721.