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

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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. For two groups of polymer blend a mixture of polyvinylidene fluoride (PVDF), polymethyl methacrylate(PMMA) and polyanylene (PAni) was used.The first group is used with various weight fractions (1,3,5) % of (PAni)while second group (10%, 30%, and 50%) of PVDF is used via solution casting method. The carried out tests are the AFM , FTIR ,SEM as well as analysis of electrical conductivity .Results illustrated that the dielectric constant was observed to saturate at mid frequency (10^3 – 10^5) Hz. At low frequency (10^1 Hz), Cp , dielectric constant and impedance resistance observed 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. Apparently, the AFM results demonstrate the topographic of neat PMMA where bigger globules are seen while little amounts of these globules is noticed in the ternary blend PMMA-PVDF– PAni. AFM micrograph of ternary blend demonstrates that the expansion of PVDF wt. % in the blend gives a decline in straightened globules as well as in the second group the ternary blends more smoother than neat PMMA . 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 1730cm−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 .As well as 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

Introduction

Since the disclosure of characteristically conducting polymers around three decades back, this particular type of polymers has gotten 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 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 target on development advanced morphologies to produce highly conductive materials where PMMA, PVDF and PAni blended in two groups. Morphology, topography and electrical properties were characterized.

Materials and Methods

Polyvinylidene fluoride, (PVDF) is 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, FTIR tests. PMMA with a density (1.18g/cm^3) and particle size of (14.59 μm) has been supplied by Sigma Aldrich Inc. Korea . PANI-W100 water dispersed with particle size about 25nm and Panichem Co. Ltd. Korea supplied diameter 20nm. DMF was supplied by central drug house CDH (P) Ltd. India.

Preparation procedure

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

Experimental Studies

D.C electrical studies were analyzed using casted film by the vertical thickness of the substrate atmosphere temperatures utilizing a Keithley electrometer type 6517. The specimen was set between two samples holders and a DC voltage is 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 they are averaged to represent this sample.

the microstructural analysis were 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.

Electrical studies

Impedance value , Cp, Dielectric Constant for two groups of polymer blend has been calculated for first group with different weight fraction of PAni (1,3,5)% as shown in table 1, and second group with different weight fraction of PVDF (10,30,50)% as shown in table2 at various frequencies as shown in figures (1-12) , respectively . Three categories of frequencies in this test are used which are : low, medium and high frequency which range between (10^1 - 10^3 Hz), (10^3 – 10^5 Hz) and (10^5 - 10^6 Hz) respectively. It can be noticed from 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 – 10^5 Hz), before diminishing progressively at high range of frequency 10^5 - 10^6 Hz. At low range (10^1 Hz) the PVDF chain structure, undergo orientation polarization, which lead to permanent dipole moment in 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 figures (2,5,8) respectively [6]. Moreover ,after chosen the optimized samples from both groups it could be observed that the Cp ,dielectric constant and impedance resistance value was decreased faster for group PMMA-30%PVDF-5%PAni than PMMA-50%PVDF-5%PAni as revealed by figures (3,6,9) respectively. This decrease in values of Cp , dielectric constant and impedance resistance is due to increase concentration of PVDF in PMMA-50%PVDF-5%PAni and PVDF has extraordinary potential in insulating and increasing dielectric constant because it has high dielectric constant consequently increasing Cp [7]. Moreover, the relationship between capacitance and dielectric constant is positive where Cp increased with increasing dielectric constant and as shown in figure 1&2 Cp and dielectric constant of PMMA-50%PVDF-5%PAni is higher than PMMA-30%PVDF-5%PAni .

Figures (10,11,12) represent electrical conductivity variation with frequency for both groups and for selected samples PMMA-30%PVDF-5%PAni and PMMA-50%PVDF-5%PAni where electrical conductivity increased with increasing frequency where the sample shows percolation thresholds at small concentration of PAni (1-5) wt.% which agreed with research [7]. Moreover the conductivity of PMMA-30%PVDF-5%PAni is higher than PMMA-50%PVDF-5%PAni cause the increasing of weight fraction of PVDF in PMMA-50%PVDF-5%PAniwhich agreed with previous research [8].

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

Table1: First groups of samples

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

Table2: Second group of samples

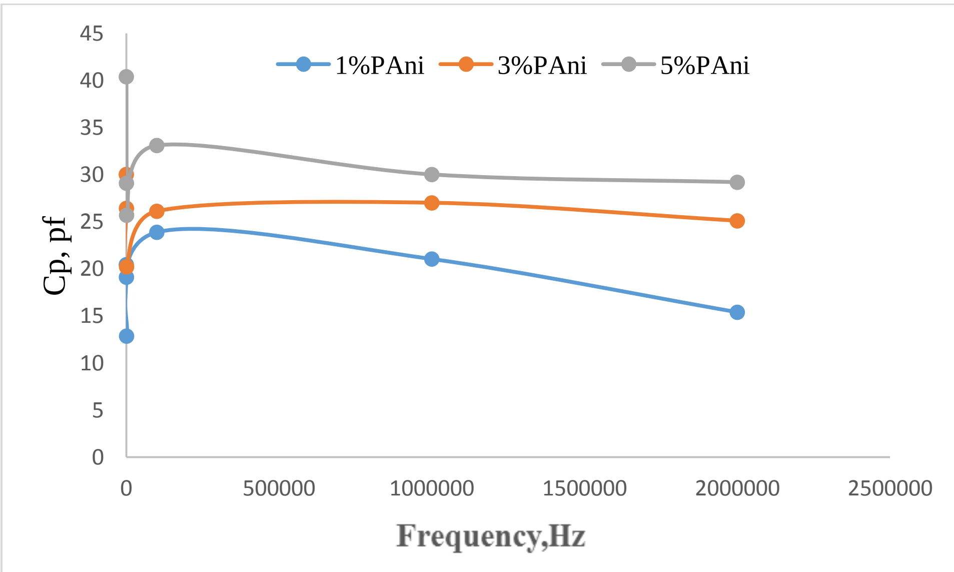

Figure 1: Variation of Cp with Frequency for various wt. % of PAni

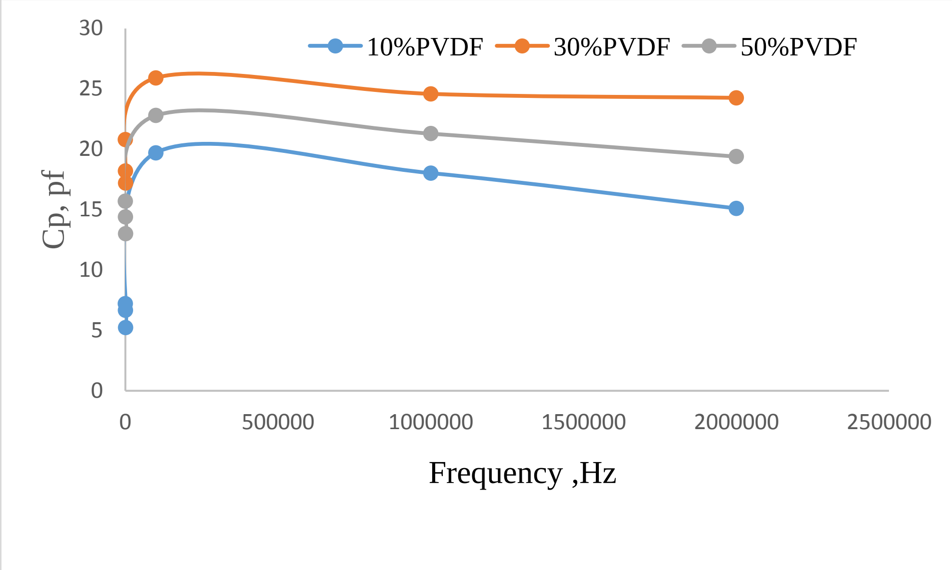

Figure 2: Variation of Cp with Frequency for various wt. % of PVDF

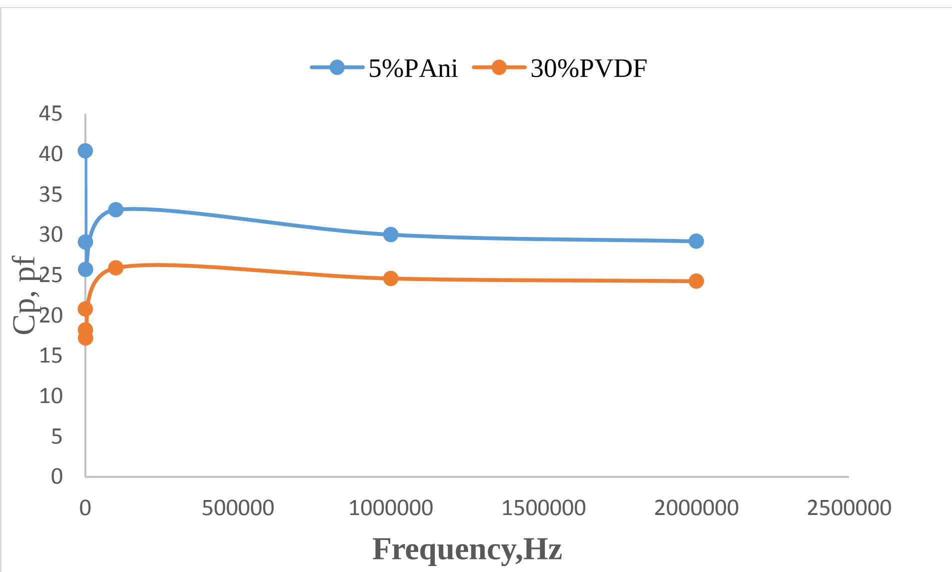

Figure 3: Variation of Cp with Frequency for optimized specimens

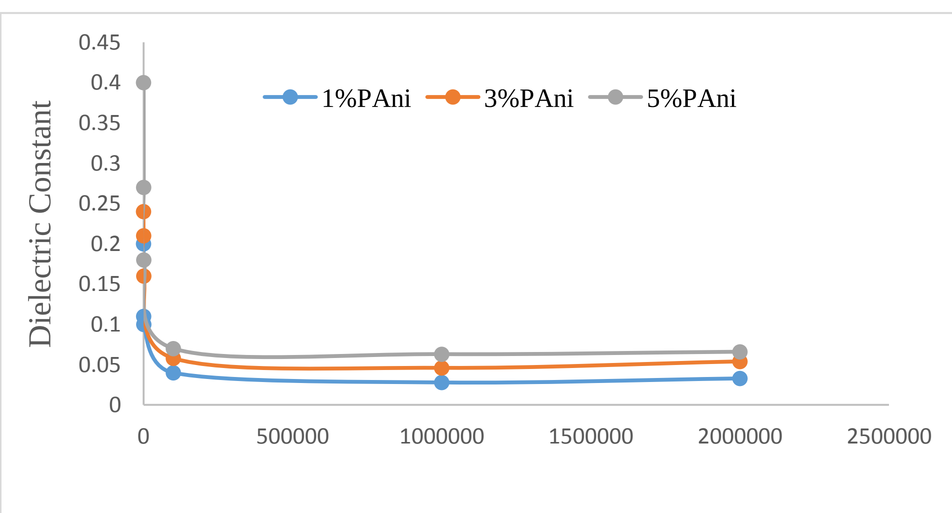

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Figure 4: Variation of dielectric constant with Frequency for various wt. % of PAni

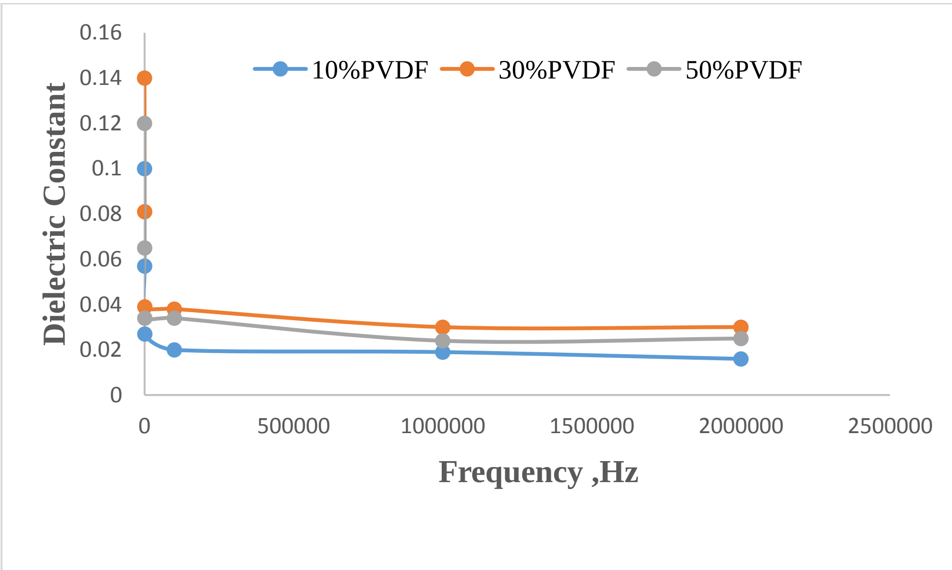

Figure 5: Variation of dielectric constant with Frequency for various wt. % of PVDF

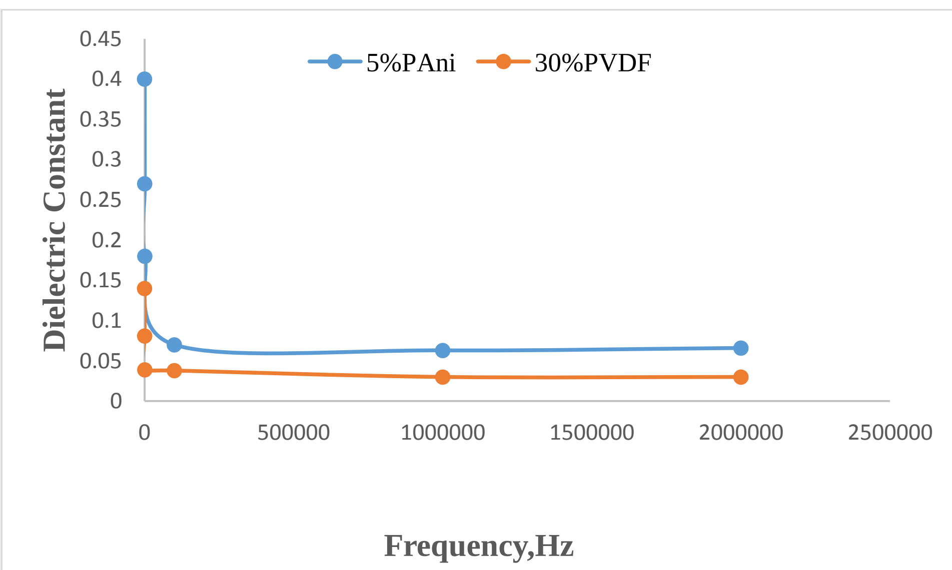

Figure 6: Variation of dielectric constant with Frequency for optimized specimen

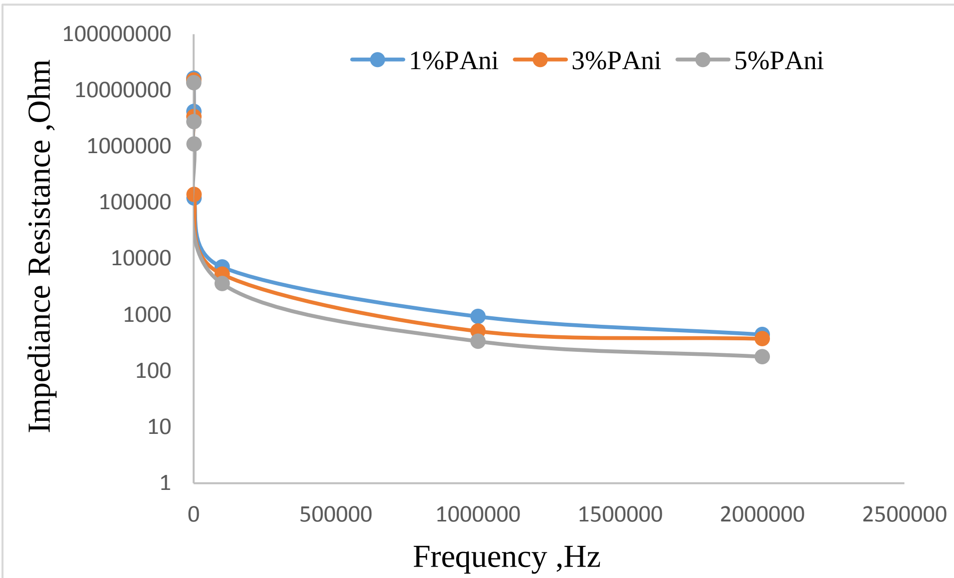

Figure 7: Variation of Impedance resistance with Frequency for various wt. % of PAni

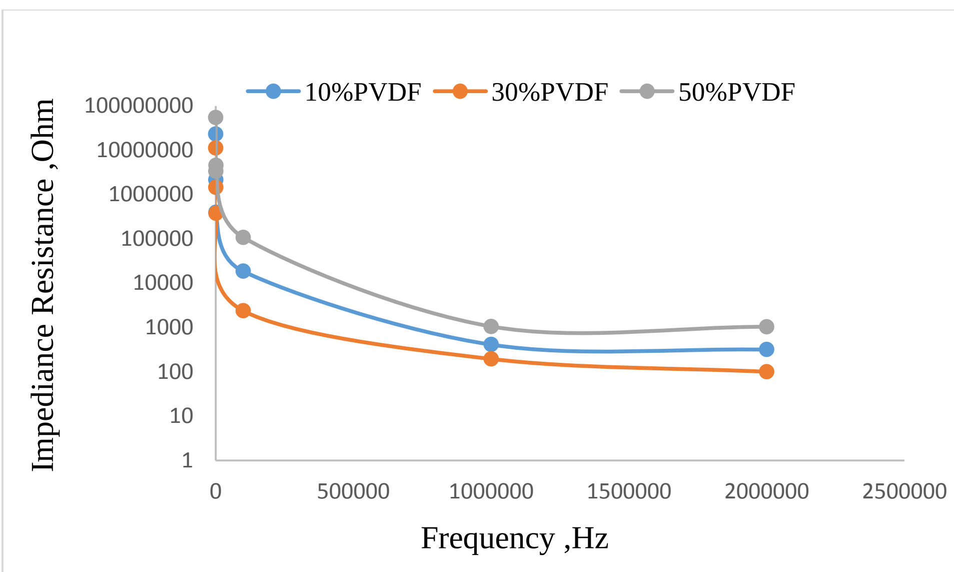

Figure 8: Variation of Impedance resistance with Frequency for various wt.% of PVDF

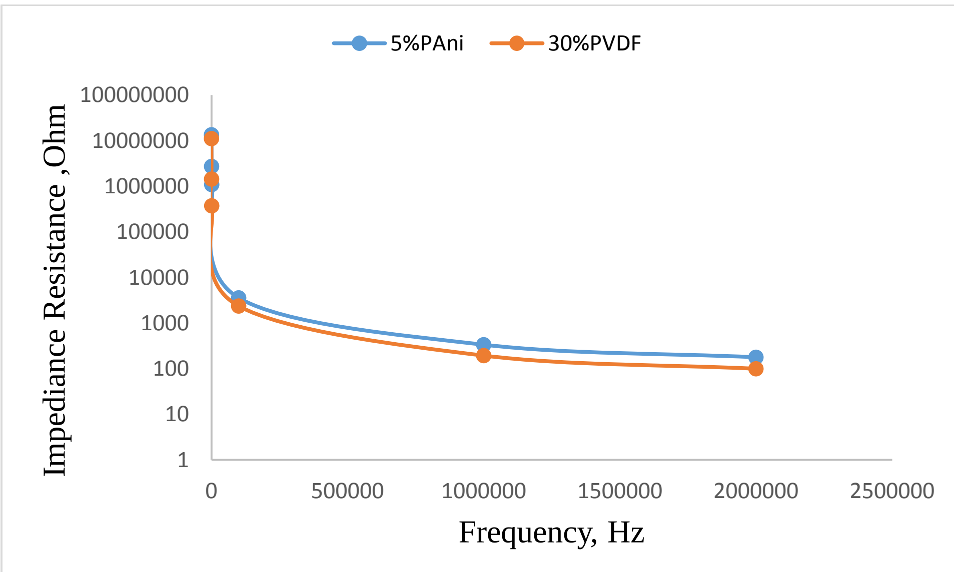

Figure 9: Variation of Impedance resistance with frequency for optimized specimens

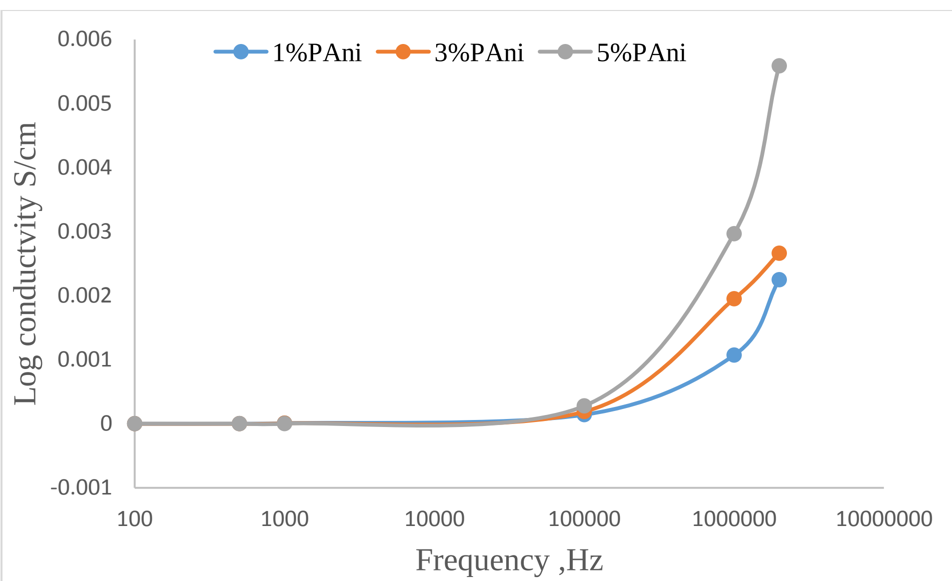

Figure 10: Electrical conductivity as a function of frequency for various wt.% of PAni

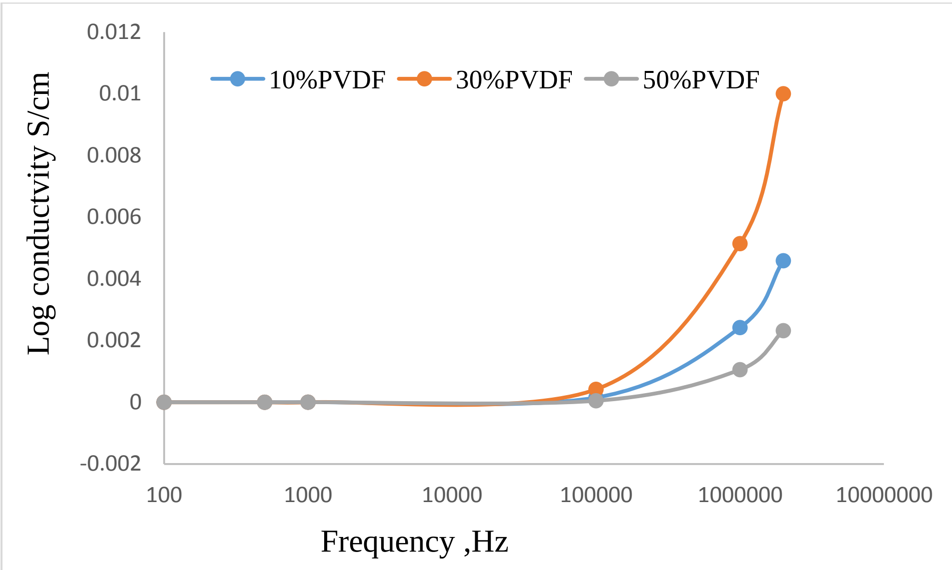

Figure 11: Electrical conductivity as a function of frequency for various wt.% of PVDF

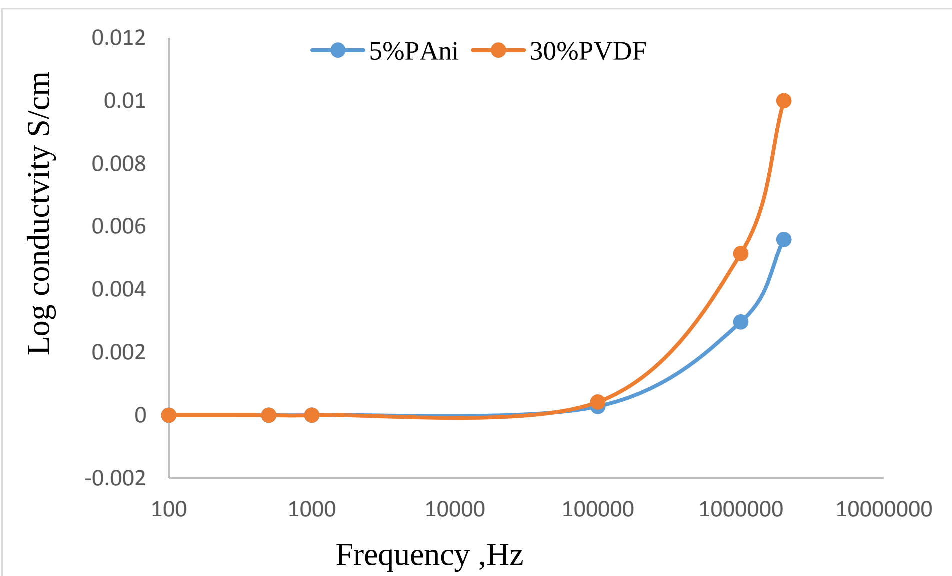

Figure 12: Electrical conductivity as a function of frequency for optimized specimens

FTIR Studies

FTIR analysis was utilized to demonstrate the structural analysis of pure PMMA and ternary blends of PMMA/PVDF/PAni as revealed by Fig. 13 which were assessed in the scope of 4200–500cm^{-1} . The absorption spectra of PANI for the prepared samples at 14010cm^{-1}corresponds to extending of (CH2),while the medium bands at 1309 and 1226cm^{-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 at1426cm^{-1} corresponds to bending and swaying of (CH2). The vibrational band at1406$cm^{-1}$is due to stretching of the antisymmetric C –C bond and at 1383$cm^{-1}$is due to stretching of asymmetric CF2 ,while at 1214 $cm^{-1}$is referred to wagging of (CH2) . The vibration modes due to stretching symmetric CH2 twisting of CH2 is appeared at 1184cm^{-1},the peak at 1152$cm^{-1}$is assigned to roking of CF2 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 CF) , wagging and bending of CF2[9]. The characteristic band for the neat PMMA is illustrated at 1449cm^{-1} for twisting of (O CH3) ,at 1487cm^{-1} is refer to scissoring of (CH2), 1066 cm^{-1} is corresponds to extending of (symmetric C- C) [10]. The higher vibration bands in the ternary blend is due to C -O group .the little movment of peaks 1728 from 1731cm^{-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 reveales the structure of the prepared ternary blend in group 1&2 . Moreover , the functional groups have the great effect on enhancing electrical and thermal conductivity of polymer composites .Results show no change was appeared in chemical structure [11]

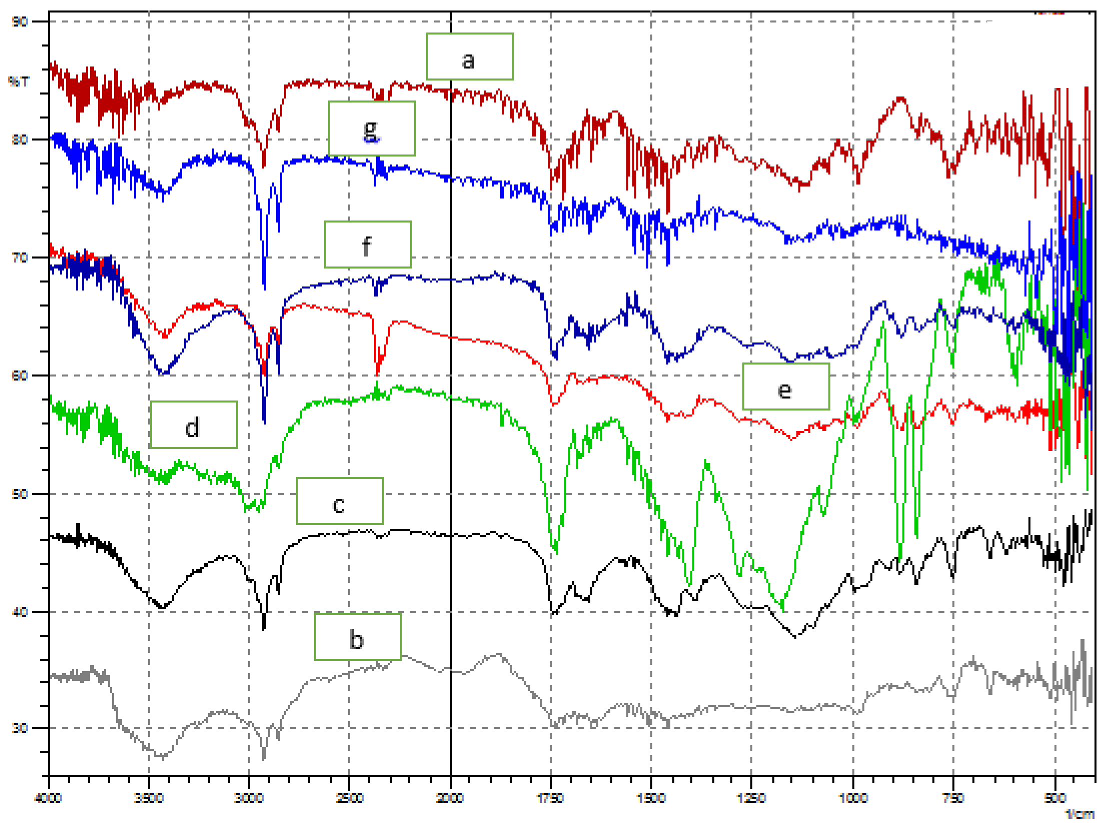

Figure13: FTIR Spectrum of ternary blend group 1and group 2 as a function of wavelength.

a. Pure PMMA b.10%PVDF c.30%PVDF d.50%PVDF e.1%PANI f. 3%PANI g.5%PANI.

Atomic force microscopy (AFM) Analysis :

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

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

Percentage	Root mean square Sq (group 1)	Root mean square Sq (group2)
Pure PMMA	64nm	
1%PAni	30.9nm	
3%PAni	25.7nm	
5%PAni	21.7nm	
10%PVDF		31.8 nm
30% PVDF		46.5 nm
50% PVDF		22.7 nm

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

AFM images of second group show the same behavior as shown in Fig 15 from AFM image, it is clear that are ternary blends smoother than pure PMMA as it is clear from fig.14 and 15, which can 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 have been altered by adding PAni, which results in development of the PAni accumulation in the fissure or pits of PMMA and PVDF, along these lines smoothing out the specimens surface and lessening the roughness as illustrated in table 3, which is clear that changing the PAni concentration affect the surface roughness of the first group samples. However, the presence of this different phase of PAni does not reject the PAni arrangement in a thin subsurface layer of the PMMA matrix [13].

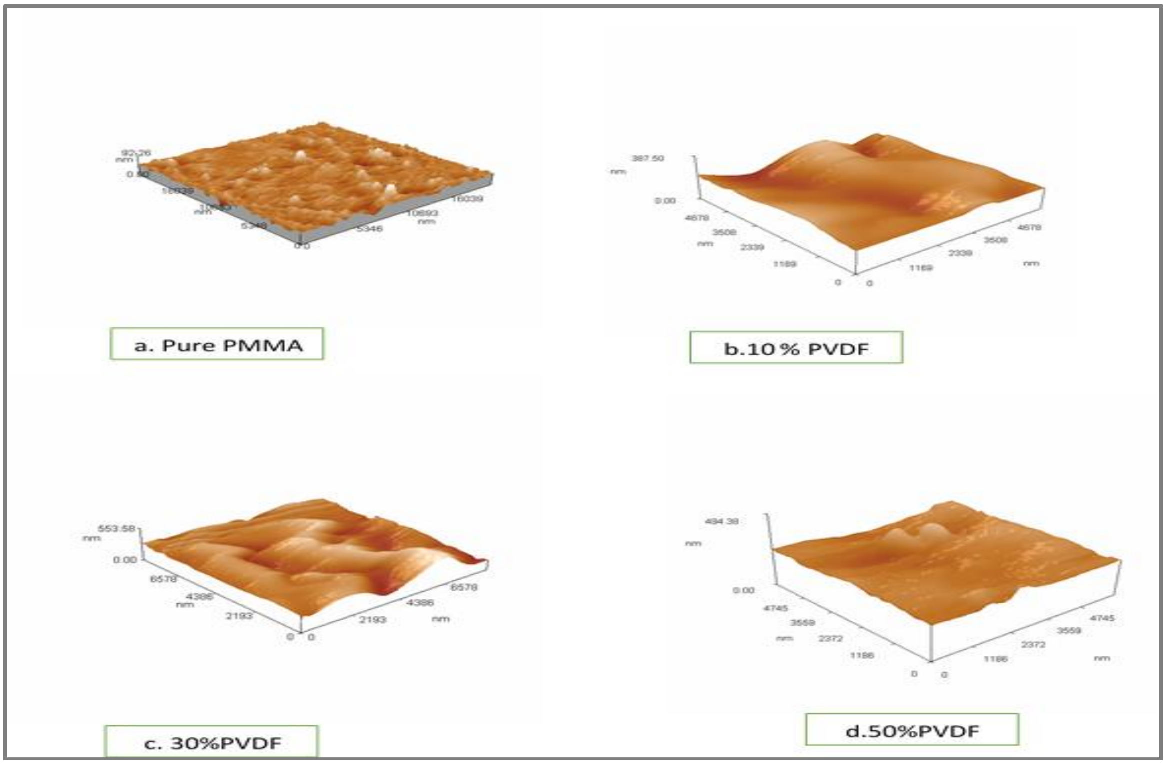

Figure 14: AFM image for group 1 of pure and ternary blends.

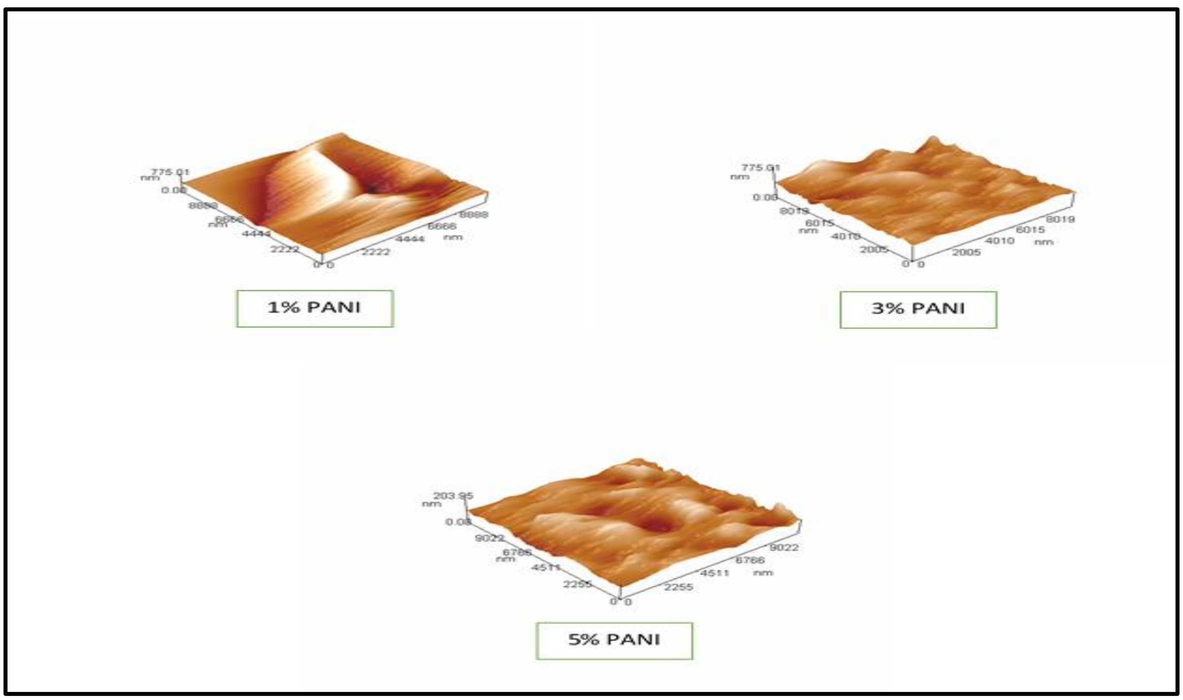

Figure 15:AFM image for seconed group of ternary blends.

Microstructural analysis (SEM)

The morphology of prepared ternary blend are represented by a sample from first group which is (PMMA-30%PVDF-5%PAni) and a sample from the second group is(PMMA-50%PVDF-5%PAni) .These samples were examined utilizing SEM technique . Figure 16 and 17 distinctly affirms that in a triple-permeated structure with PAni as the internal phase, PAni will disperse. As appeared in Figure (16, a ,b ,c ,d) 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 arrange in within and outside and PVDF situates at the interface. Because of the lower interfacial tension among PVDF and PAni results in the interfacial adhesion of the whole PAni and PVDF in one another, and the development of little phase sizes. Besides as appeared by figure (16 a, b, c, d) that when the concentration of PMMA is higher the PAni arrange is better and uniform with homogeneous branches circulated all through the sample. As shown in figure17 B ,C and D, in 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 appeared in Figure 16 a, b, c and d the quantity of huge PVDF islands lessens. These vanishings of huge PVDF parts proceed with the decrease of the concentration of PVDF until no large PVDF parts are watched. 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 tends to be presumed that a standout amongst other methods for decreasing the permeation threshold, in spite of double percolated structure, is involving places with different component. In a PMMA-50%PVDF-5%PAni blend, the zone involved by PAni has been restricted as it is cleared in figure 17 C and D cause of persistent phase of PVDF and PMMA, and substantial PVDF zones when contrasted with the counterpart group. These outcomes in a lower permeation threshold of PAni, and an expansion in the conductivity of the sample [14, 15], as revealed by impedance resistance of the samples Figure3.

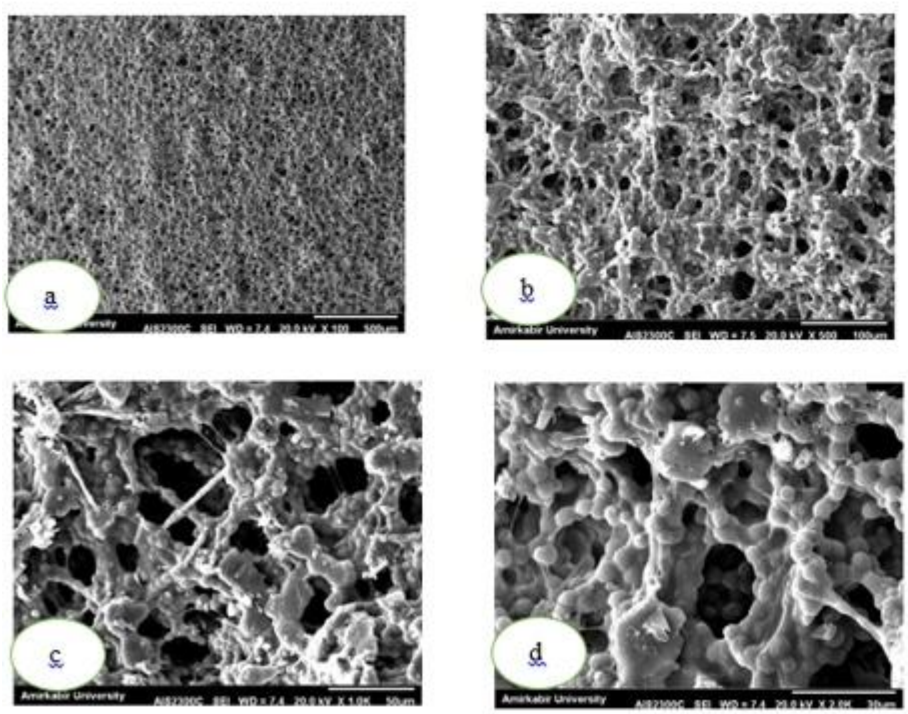

Figure16: SEM image of fractured surface of samples as a function of PVDF wt. %, PMMA-30%PVDF-5%PAni

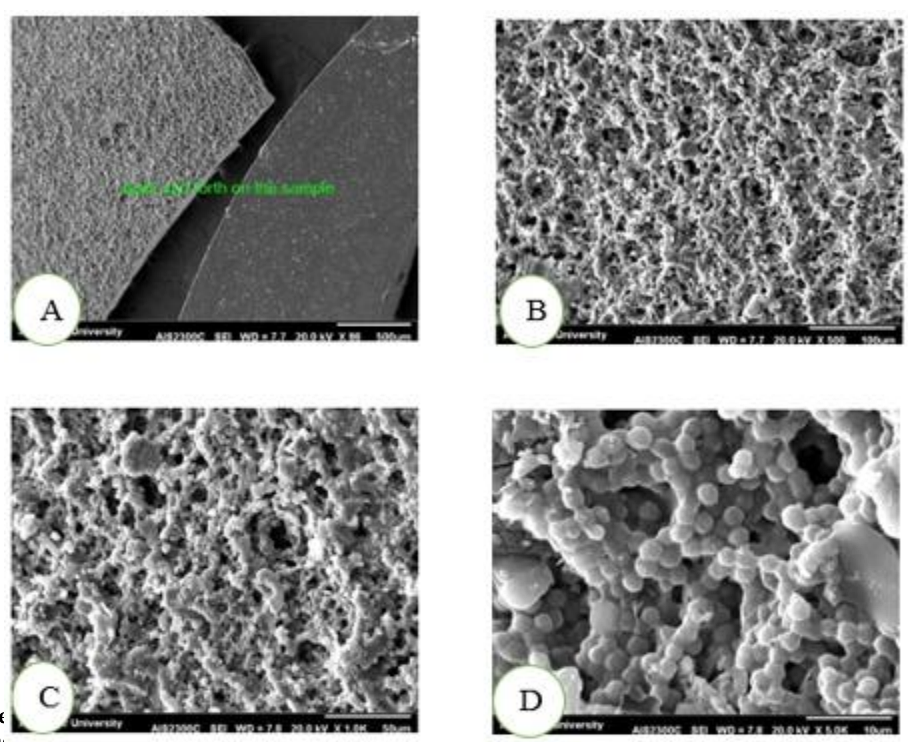

Figure17: SEM image of fractured surface of samples as a function of PVDF wt. PMMA-50%PVDF-5%PANI

Conclusion

The objective of this work is to develop multi-component phase morphology of blends. This morphology is performed by fabricating two groups of PMMA/PVDF/PAni ternary blends using solution-mixing method. This research aim to evaluate the triple-percolated morphology to decrease the percolation threshold of all phases in the prepared blend. Results showed that dielectric constant is saturated at mid frequency (10^3 – 10^5) Hz. At 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 provides a decrease in smoothened globules as well as in the second group the ternary blends smoother than neat PMMA. The entire arrangement of our outcomes shows relationship between the structure and electrical properties of PMMA– PVDF– PAni ternary blends. SEM image illustrated homogenous mixing for both groups and in a(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) .

References

[1] Fratoddi, Venditti, Cametti, Russo M.V. , 2015. Sensor Actuator B Chem 220:534-548. doi: 10.1016/j.snb.2015.05.107.

[2] Luiz F. Malmonge , Giovana de A. Lopes, Simone do C. Langiano,José A. Malmonge, Joo M.M. Cordeiro, Luiz Henrique C. Mattoso, 2006 . European Polymer Journal. 42 3108–3113.

[3] A. K. Tomar , Suman Mahendia, Rishi Pal Chahal and Shyam Kumar, 2011. AIP Conf. Proc. 1393, 145; doi: 10.1063/1.3653651.

[4] Ravati Sepehr, 2010 .thesis submitted to university of De Montreal.

[5] Ievgen Duboriz and Alexander Pud, 2014 . Sensors and Actuators B: Chemical. 190, 398–407.

[6] M.D. Rozana, A.N. Arshad, M.H. Wahid, M.N. Sarip & M. Rusop, 2017. International Journal of Research in Science (ISSN Online: 2412-4389) IJRS ,3 ,1. DOI: 10.24178/ijrs..3.1.08.

[7] Malmonge LF, Mattoso LHC., 1995. Polymer.36:245–9.

[8] Shiyong Yang and Eli Ruckenstein, 1993 . *Synthetic Metals. 59* , 1-12.

[9] Sudip Ray, Allan J. Easteal, Ralph P. Cooney, Neil R. Edmonds, 2009 . Materials Chemistry and Physics. 113 , 829–838.

[10] Jin-Woo Park,Yun-Ah Seo,Il Kim, and, Chang-Sik Ha, Keitaro Aimi and, and Shinji Ando, 2004 . Macromolecules . 37 ,2,, 429-436 ,DOI: 10.1021/ma035402g.

[11] Supri A. Ghani and Heah Chong Young**,** 2010. Journal of Physical Science, 21,2, 81–97.

[12] Nizamara S. Pereira, Maria J. A. Sales, Artemis M. Ceschin, , 2012. Polímeros . 22, 4, 384-389.

[13] V.N. Bliznyuk, A. Baig, S. Singamaneni, A.A. Pud, K.Yu. Fatyeyeva, G.S. Shapoval, 2005 .Polymer, xx ,1–9.

[14] Zilberman, M., Siegmann, A., & Narkis, M. ,2000. Journal of Macromolecular Science – Physics. B39,3, 333-347.

[15]Yuan, Z., & Favis, B. D. ,2006. Journal of Polymer Science, Part B: Polymer Physics. 44,4, 711-721.