Thermal and Dielectric properties of PVC/PMMAloaded conductive PPY composites

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Abstract: Thermal properties of the PVC/PMMA loaded conductive polypyrrole composites were analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). A decrease in the glass transition temperatures T_g with the conductive PPy concentration content reveals the increase of segmental motion. Dielectric properties of these composites were studied in the frequency range between 100 Hz and 5 MHz at room temperature for various weight percentage of conductive PPy. The x-ray diffractograms of all the samples ensures the amorphous nature of the composites.

[G. M. Nasr, H. M. Osman, M.M. Omar and A.M. Abd Elbary. **Thermal and Dielectric properties of PVC/PMMA loaded conductive PPY composites.** *Life Sci J* 2014;11(4):127-134]. (ISSN:1097-8135). http://www.lifesciencesite.com. 17

Key words: Composites, dielectric properties, thermal properties, conducting polymer

1. Introduction:

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials(1).A large amount of work has been reported on the conduction mechanism in polymeric materials. The electrical conduction in polymer film has much importance due to the discovery of the memory phenomenon (2) and has wide applications now-a-days in thin film devices (3). In recent years, because of the need for electrostatic charges dissipation, electromagnetic shielding etc., new polymers with appreciable electrical conductivity have been formulated. Before 37 years Schurer *et al.*(4) studied the addition of methyl methacrylate and its polymer (PMMA) to improve the thermal and mechanical properties of PVC. Deshmukh*et al.*(5) reported electrical conduction in semiconducting PVC–PMMA thin film. The wide spread use of PVC is attributed mainly to its high electrical and chemical resistance and its unique ability to be mixed with additives to produce a large number of compounds with wide range of physical and chemical properties (6). Thermal properties of the polypyrrole-poly (methylmethacrylate) (PPy)-(PMMA) composites were analyzed by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC)byAchour*et al.*(7).

Despite the polar nature of polyvinylchloride (PVC), it is used at large scale as an insulating material because of the constancy of its dielectric properties. Poly(methyl methacrylate) (PMMA) is a hard, rigid, transparent thermoplastic, which has good outdoor weatherability and is more impact resistant than glass. PMMA is weakly polar. When it is blended with PVC, the dielectric constant shows no large variation with temperature in the maximum-use temperature range. The present study discusses the electrical and thermal properties in conductive PPy filled PVC/PMMA thin film thermoelectrets. Since PVC is proton donor and PMMA is proton acceptor selected as basic polymeric materials. The choice of these polymers is taken into account for the donor acceptor capabilities.

This work presents a study on the dielectric and thermal, that is thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) properties of the composites made up of conductive polypyrrole (PPY) particles in an insulating matrix of poly vinylchloride (PVC) /poly methylmethacrylate (PMMA). The first objective of this work is to analyze these composites by calculating dielectric constant in the frequency range of 100 Hz to 5MHz. The observed dielectric response of the composites will be examined using the proposed model of **Ezzat***et al.***(8)**. The second objective is to study the influence of load factor (PPY) on some thermal properties.

2.1.Material and Method of preparation.

Polyvinylchloride (PVC) of standard grade supplied by Fluka, and poly(methyl methacrylate) (PMMA) supplied by Alfa Aesar, were used for the study. The conducting polymer (polypyrrole) was also supplied by Aldrich.

For the preparation of polypyrrole doped thin film, the two polymers, PVC (1.5 g) and PMMA (0.5 g), were taken in the ratio 3: 1 by weight, 1.5 g of PVC in 15 ml of tetrahydrofuran (THF) and 0.5 g of PMMA in 5 ml of THF dissolved separately and subsequently mixed together. Polypyrrole was taken in different wt % and was dissolved in 5 ml of THF to produce polypyrrole solution. After allowing them to dissolve completely, the three solutions were mixed together. The solution was slightly heated to allow polymers to dissolve completely to yield a clear solution. A glass plate thoroughly cleaned with hot water and then with acetone was used as a substrate. The solution was poured on the glass plate and allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber maintained at a room temperature (25°C). In this way, the film was prepared by isothermal evaporation technique. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities.

2.2. Electrode coating

The electrode coating on the film of measured thickness was done by using quick drying and highly conducting silver paint supplied by TAAB. A mask of circular aperture of 1.0 cm diameter was used while coating, to ensure uniformity in the size of the coated silver electrode.

2.3. Structural characterization

For structural characterization the x-ray diffractograms of PPy filled PMMA: PVC films were obtained on XPERT – PRO – PAN analytical – Netherland. The x-ray diffractograms of all the samples ensures the amorphous nature.

2.4. DSC and TGA measurements

The DSC was carried out using a Shimadzu DSC-50 differential scanning calorimeter programmed between 20 and 450°C atheating rate of 10°C/min and under nitrogen flow of 30 ml/min. The sample was placed in an aluminum cell or plate with a lid and the reference cell was empty. TGA was carried out using a Shimadzu TGA-50 Thermo gravimetric analyzer. The measurements were taken under an atmosphere of nitrogen with a flow rate of 30 ml/min, at temperatures between 20 and 450°C and a heating rate of 10 °C/min.

2.5. Dielectric measurements

The dielectric properties were measured using a bridge (HIOKI 3538-50 LCR Hi Tester) in the frequency range 10^2-10^6 Hz. The crosslinked samples were in the form of disks of 0.1-0.2 cm thick and 1.5 cm in diameter.

The dielectric constant ε'(real part of the dielectric constant) of the samples and the a.c conductivity σ_{ac} were calculated by using the relations(9)

$$\varepsilon' = \frac{d}{\varepsilon_o A} C \qquad (2.1)$$

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon'' \qquad (2.2)$$

$$\varepsilon'' = \varepsilon' \tan \delta \qquad (2.3)$$

Where C is the capacitance of the sample, d is thickness and A is the area of the sample.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC) studies.

The DSC curves of native PVC/PMMA and its conductive polypyrrole composites are plotted in Figures (3.1a & 3.1b) the corresponding thermal dynamic data values are listed in Table (3.1). The following trend is observed in all the DSC thermograms. An endothermic reaction T_g is observed which is then followed by T_m (melting temperature) and decomposition temperature T_d upon heating the samples further. Apparently, only one T_g is displayed for PVC-PMMA polymer blend and this indicates the homogeneous behaviour of the polymer blend. The determination of the glass transition temperature was carried out according to the method of the tangents (10).

In addition T_g decreases upon incorporation of PVC due to the interaction between PMMA and PVC via crosslinking. In contrast, T_m has been found to fall in the range of T_m values of PMMA and PVC as well as T_d values. One distinct endothermic peak T_m is illustrated in Figure (3.1a). This broad peak is due to the overlapping of the melting points of PMMA and PVC. Two endothermic peaks are observed thereafter.

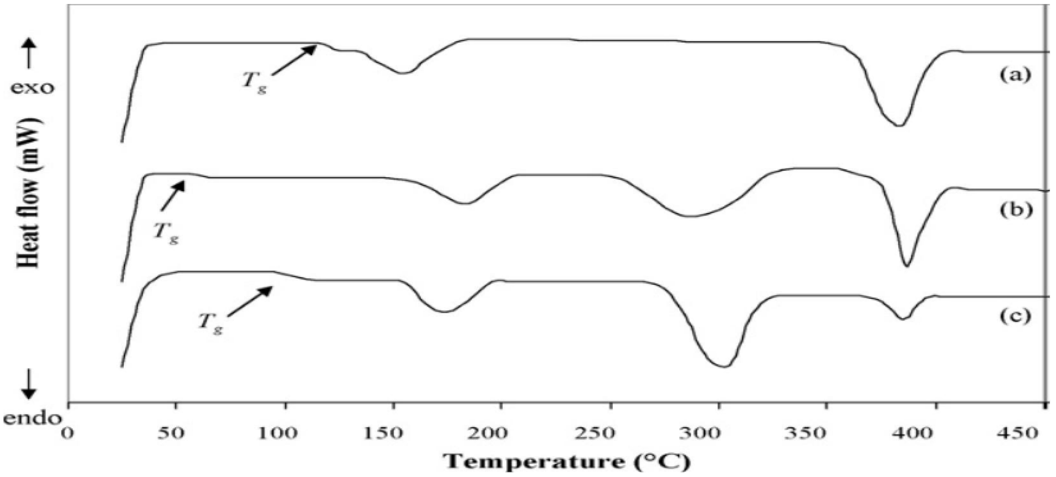

Figure (3.1a): DSC thermograms of (a) pure PMMA, (b) pure PVC and (c) PMMA–PVC.

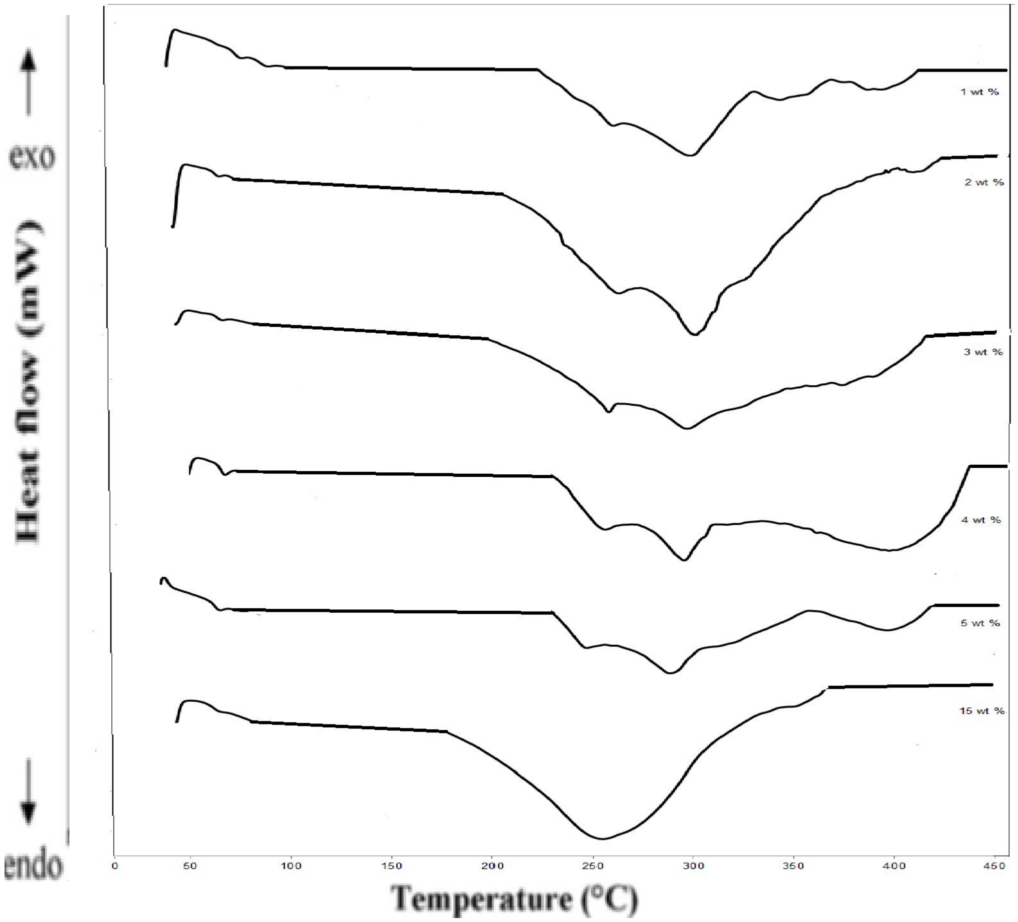

Figure (3.1b): DSC thermograms ofall PVC/PMMA loaded conductive polypyrrole composites.

These peaks are known as decomposition temperature T_d. The first intense peak is related to the dehydrochlorination of PVC$^{(11)}$, whereas the degradation of unsaturated group of PMMA and the degradation of PVC contribute to second endothermic decomposition peak $^{(12)}$. As shown in Figure (3.1 b), a single value for T_g is obtained for all PMMA/PVC loaded samples and its value decreases with the addition of conductive polypyrrole till 4 wt. % contents and then began to increase with further loading of polypyrrole.

Meanwhile, PMMA/PVC sample loaded with 1 wt % of conductive polypyrrole shows two values of T_g corresponding to the T_g values of PVC and PMMA, respectively. It shows the phase separation is mainly due to the slow evaporation of polymer solutions during preparation. Polypyrrole conductive agglomerates seem to form blocking region whichreduces the flexibility of polymer chain and contributes to the lower segmental motion of polymeric chain. T_m value decreases with addition of polypyrrole contents as shown in Table (3.1).

Table (3.1): Shows the Thermal dynamic data values of filler composites.

Weight % of Polypyrrole	Glass temperature T_g (°C)	Melting temperature T_m (°C)	Decomposition temperature T_d (°C)
Zero wt. %	66.23	287.69	415.95
1 wt. %	63.27 ,77.09	292.20	337.13
2 wt. %	52.08	253.47	292.01
3 wt. %	62.34	253.91	293.36
4 wt. %	61.61	254.01	293.63
5 wt. %	65.76	252.79	363.14
15 wt. %		252.89	

3.2. Thermogravimetric analysis (TGA) studies (13)

Thermogravimetric analysis of pure PMMA, pure PVC, PMMA/PVC blend and PMMA/PVC loaded conductive polypyrrole are depicted in Figures (3.2a) & (3.2b) respectively. Based on the TGA curves, all samples have shown 3 stages, except for pure PMMA compound. The initial weightloss of 4 % at 167 °C for pure PMMA and weight loss of 2 % at 148°C for pure PVC samples illustrated in Figure (3.2). However, PMMA/PVC blend has a weight loss of 13% at 220°C.

Meanwhile the weight loss for loaded PMMA/PVC approximately decreases with polypyrrole loading at 200°C. a dramatic drop in weight is observed for the second weight loss. The pure PMMA sample loses 82% weight at 387°C with residual mass of 11%. On the contrary, after complete dehydration, the second and final weight loss of PVC is 52% at 256°C and 6% at 336°C respectively. The second weight losses for PMMA/PVC loaded polypyrrole samples starts at approximately 200°C and end at 370°C and the final weight loses of 47% - 63% is detected from unloaded samples to the sample loaded with 4 wt % polypyrrole. Samples loaded with 4wt. % and 15 wt. % exhibit only two stages of weight losses. A gradual fall in weight loss is following the second stage of weight loss. The residual weight after final stages (as depicted in Table (3.2)) is gradually increases by polypyrrole loading up to 15 wt %. The sample loaded with 4 wt % represent two stages of weight losses and remarkable weight loss with respect to the other samples. Based on the TGA curve, the initial weight loss of this sample is around 11% which starts at 93°C followed by a weight loss of 62% which starts at 210°C until 448°C. at 448°C, the residual weight of this sample is still around 25%.

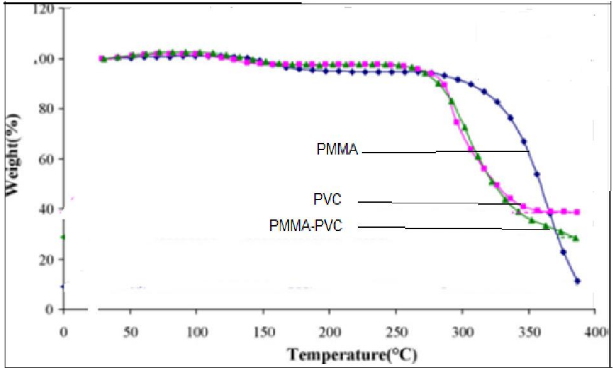

Figure (3.2 a): TGA thermograms of PVC, PMMA and PVC/PMMA.

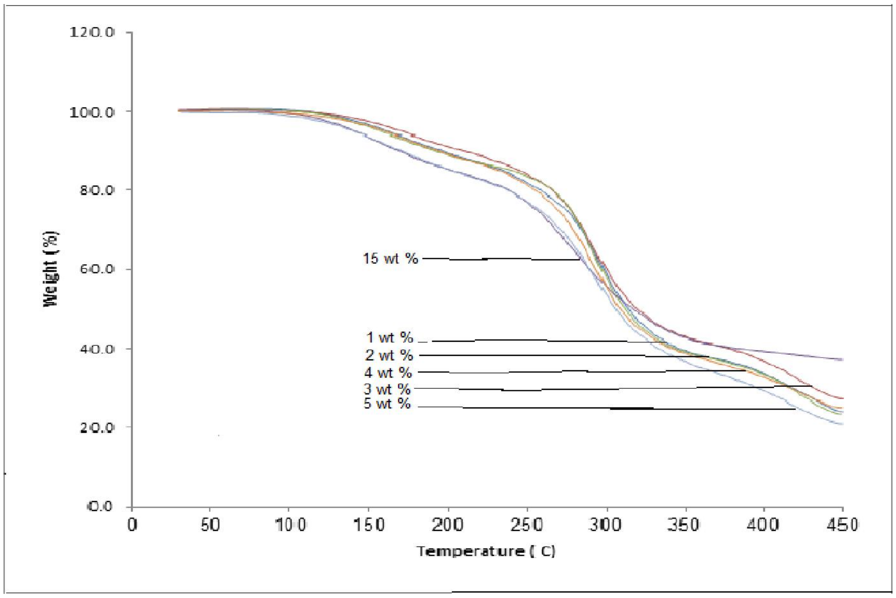

Figure (3.2 b): The TGA thermograms of PVC/PMMA loaded PPy composites.

Table (3.2): Shows the Maximum degradation and Residue % of filler composites

Weight % of Polypyrrole	Maximum Degradation T_{max}	Residue (%)
Zero wt. %	283.09	74.348
1 wt. %	290.18	76.851
2 wt. %	294.32	76.323
3 wt. %	292	73.393
4 wt. %	291.18	75.020
5 wt. %	290	78.892
15 wt. %	279	63.081

3.3. XRD analysis

The x-ray diffraction is a useful tool to determine the structure and crystallization of the polymer matrices (14). In order to investigate the effect of conductive polypyrrole concentration in the PVC/PMMA system. XRD analysis has been performed, and their respective diffraction patterns of pure PVA, pure PMMA, PVC/PMMA and PVC/PMMA loaded with different concentration of conductive polypyrrole filler particles as shown in Figure (3.3).

From figure (3.3), a broad characteristic peak of PMMA was obtained at angles $2\Theta = 16.4^{o}$ with shoulder at $2\Theta = 22.5^{o}$ which reveals the amorphous phase of PMMA. The intensities of these characteristic peaks is decreased after the impregnation of PVC. This implies that the addition of PVC disrupted the arrangement in the polymer backbone of PMMA(15, 16). The presence of interaction between PMMA and PVC, such as crosslinking, is attributed to this phenomenon.

The blending of PMMA with PVC shifts the peaks at $2\Theta = 16.4^{o}$ and $2\Theta=22.5^{o}$ to17^{o} and 25.3^{o}, revealing the change in crystallographic organization (13). With the addition of conductive polypyrrole particles the two peaks shift toward higher 2Θ values which confirm the complete mixing of this filler with PVC and PMMA matrices. It can be seen by comparing Figure (3.4) with Figure (3.3 c) that the characteristic peak intensity decreases slightly upon incorporation of conductive polypyrrole.

It can be inferred from the above comparing that the degree of crystallinity decreases and hence increases the amorphous region in polymer matrix which leads to higher ionic conductivity.

3.4. Dielectric behaviour

Dielectric and conductivity relaxations are present in these composites and can be investigated by dielectric spectroscopy. However, because of the presence of conductive particles, dielectric or conductivity relaxations may be obscured, as for example in the case of interfacial polarization observed in heterogeneous systems (17).

The dielectric constant ε' versus frequency of the composites with 0,1, 2, 3, 4, 5, and 15 wt (%) in conductive polypyrrole particles is shown in Figure (3.5) at room temperature(30 °C). Dielectric constant ε', is increasing with polypyrrole content. In the low frequency region, ε' reaches value which drop to the normal values for these composites, as frequency increases, indicating the existence of dielectric relaxation. This could be discussed on the bases of the following. When conductive particles are dispersed in a non-conductive matrix, the dielectric constant of the resulting composites increases with the weight fraction of the filler, as theory predicts(18,19), and has been experimentally found (20, 21).

In the region of low frequencies, dielectric constant attains high values which decreases as frequency increases as shown in Figure (3.5). This behaviour depicts a relaxation process that must be attributed to an interfacial polarization, known as Maxwell-Wagner-Sillars (MWS) effect (22, 23), and a phenomenon appearing in heterogeneous media due to the accumulation of charges at the interfaces.

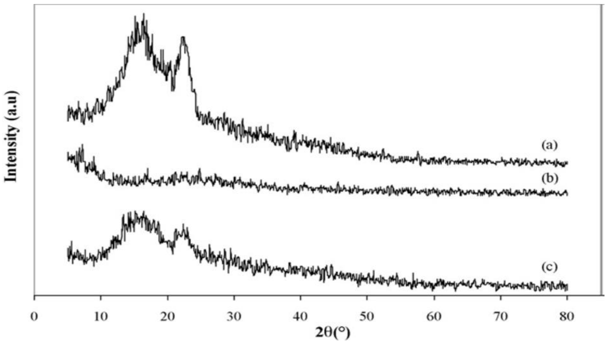

Figure (3.3): XRD patterns of (a) pure PMMA, (b) pure PVC and (c) PMMA–PVC.

To predict the interphase dielectric constant, a model proposed by Ezzat, Sabiha and Izzularab (ESI) was suggested (8).They suggested that for polymers, especially those of large molecules, formation of air voids in the interphase region is dominant as compared to the filler molecules so that, the interphase region can be assumed to consist of resin material and air bubbles. So, the interphase dielectric constant can be assumed to be function of resin and air dielectric constants only, and the interphase dielectric constant can be computed from:

$$\varepsilon_3^{\beta} = \varepsilon_2^{\beta} + \varphi_{\mathrm{a}}\left(1 - \varepsilon_2^{\beta}\right) + \varphi_{\mathrm{f}}\left(\varepsilon_1^{\beta} - \varepsilon_2^{\beta}\right) \tag{3.1}$$

Where ε_3 is the effective dielectric constant, Φ_a is the volume fraction of air;Φ_f is the volume fraction of filler and ß is a constant which can be computed from

$$\beta = 1 - 2\left[\frac{1}{1 + 1.6(a:b) + 0.4(a:b)^2}\right] \tag{3. 2}$$

For ceramic and polymers of smaller molecules, formation of air voids in the interphase region can be neglected as compared to the filler molecules so that, the interphase region can be assumed to consist of resin material and filler molecules. So, the interphase dielectric constant can be assumed to be function of resin and filler dielectric constants only, and the interphase dielectric constant can be computed from:

$$\varepsilon_3^{\beta} = \varepsilon_2^{\beta} + \varphi_{\mathrm{f}}\left(\varepsilon_1^{\beta} - \varepsilon_2^{\beta}\right) \tag{3.3}$$

Also, the effective dielectric constant of the composite can be calculated from Eq. (3.4).

$$\varepsilon_{\mathrm{c}}^{\beta} = \varphi_1\varepsilon_1^{\beta} + (1 - \varphi_1)\varepsilon_2^{\beta} + \varphi'\left(\varepsilon^{\beta} - \varepsilon_2^{\beta}\right) \tag{3.4}$$

Where Ɛ is the dielectric constant of air (~ 1) for polymers of large molecules or Ɛ is the dielectric constant of the filler for ceramics and polymers of smaller molecules. Φ′ can be computed fro

$$\varphi' = \varphi_1 \frac{1 - \varphi_1}{1 + \varphi_1} \qquad (3.5)$$

If the dielectric constant of the matrix is greater than the dielectric constant of the filler then Ɛ and $Ɛ_2$ must be reversed in the last term of Eq. (3.4).

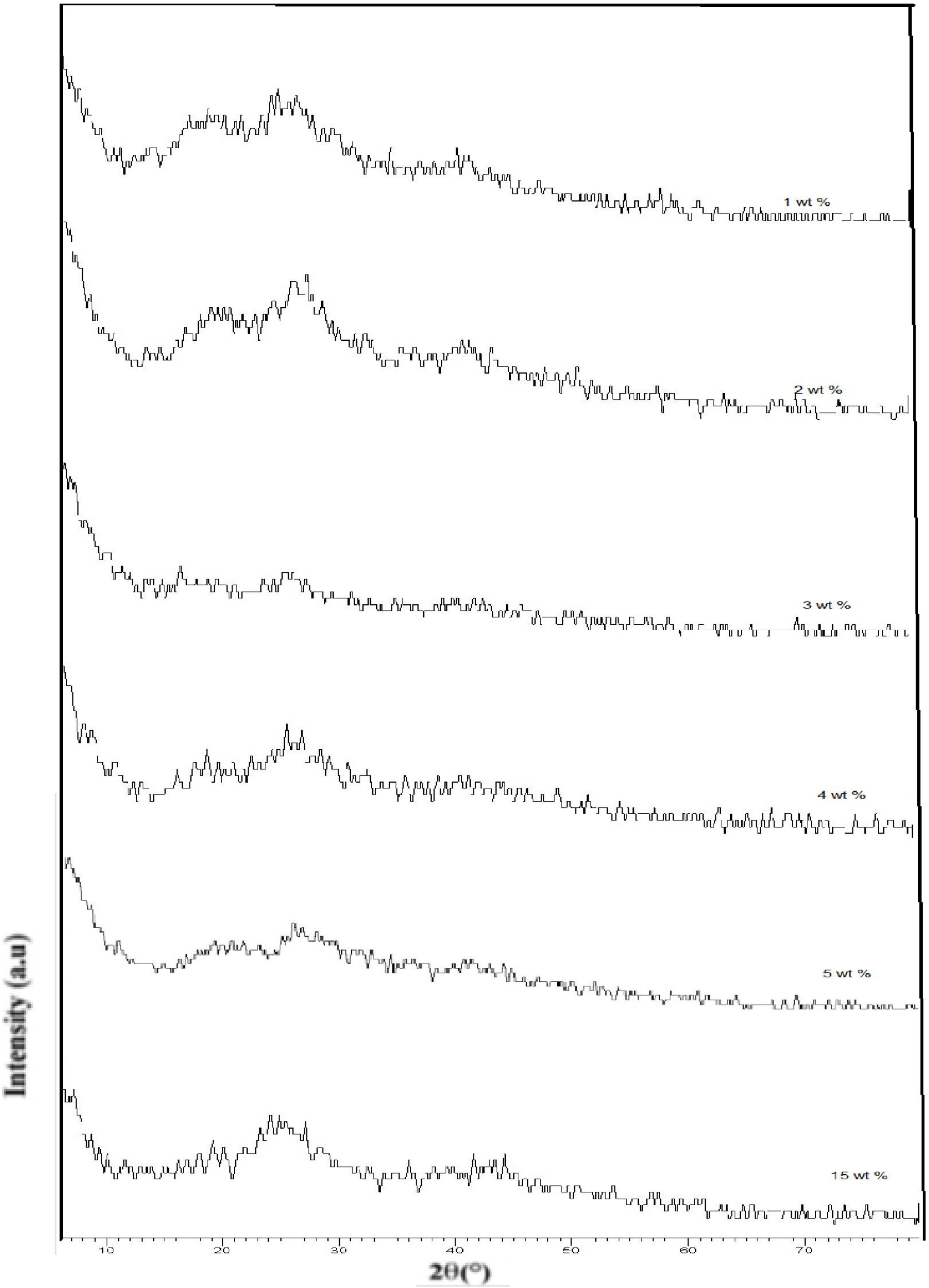

Figure (3.4): XRD patterns of conductive polypyrrole composites of PMMA -PVC.

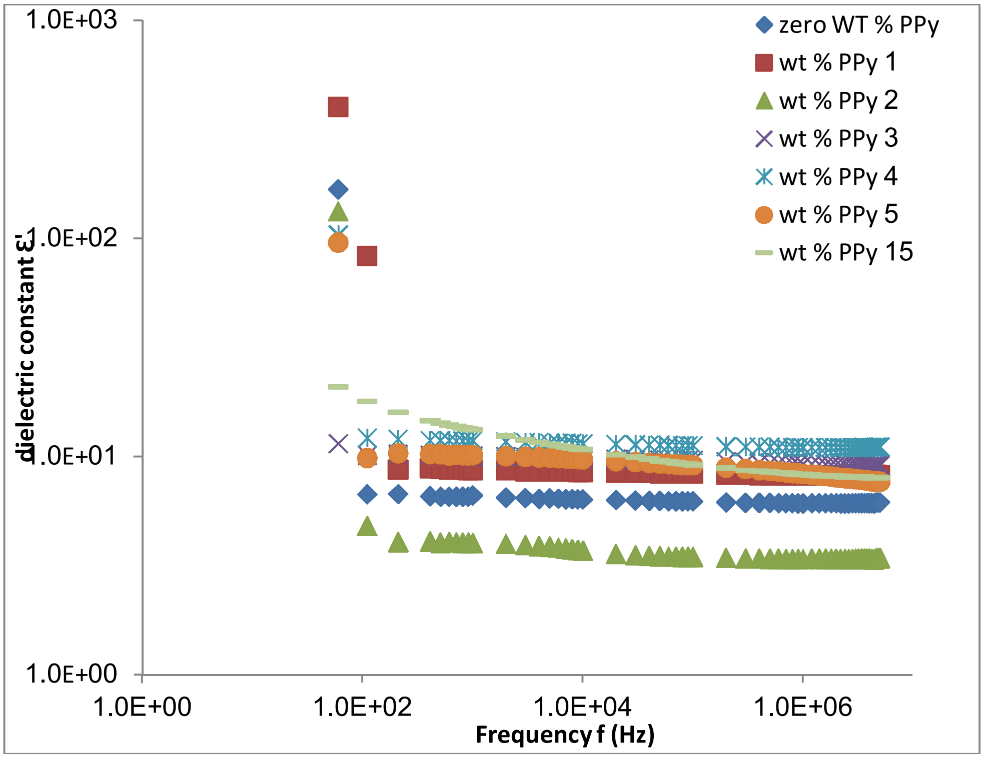

Figure (3.5): The relation between the logarithm of dielectric constant and the logarithmic frequency for all samples.

Figure (3.6) represents the experimental filler dependence of the effective dielectric constant data of PVC/PMMA composites and the corresponding calculated values on the basis of the mentioned model.

By looking at ESI model and comparing the effective dielectric constant as a function of conductive polypyrrole particle contents, one found that the ESI model gives a better accuracy.

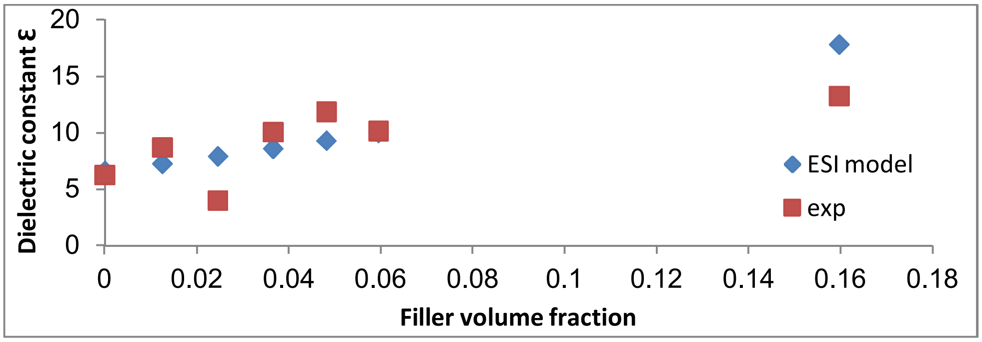

Figure (3.6): Relation between the dielectric constant and the filler volume fraction for all samples.

4. Conclusion

In this work, some dielectric and thermal properties of the composites consisting of conductive polypyrrole (PPY) particles in a poly vinylchloride (PVC)/polymethylmethacrylate (PMMA) matrix is reported. The study under thermal stress (TGA, DSC) carried out on this series of samples shows that the thermal parameters such as the glass transition temperature and the degradation rate depends on the mass concentration of conductive PPY in PVC/PMMA matrix. In addition, the dielectric study shows thatthis behaviour depicts a relaxation process that must be attributed to an interfacial polarization, known as Maxwell-Wagner-Sillars (MWS) effect, and a phenomenon appearing in heterogeneous media due to the accumulation of charges at the interfaces.

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