تأثير التغيرفي تركيزالبولي بيرول (PPy) على الخواص العزلية لشبكة البوليمر المتداخلة (IPNs) من بوليمر البولي بيرول (PPy) وبوليمر إيثيلين – فينيل– أسيتات (EVA)

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الملخص :

دراسة خصائص العزل في شبكات البوليمر المتداخلة (IPNs) مهمة جدا لأن وجود حالة تداخل لمكونات المركب PPy/EVA يؤثر بشكل كبير على حركة ناقلات الشحنة في حالة التوصيل.

في هذه الورقة البحثية تم التحقق من اعتمادية كل من ثابت العزل الكهربائي ومعامل الفقد الكهربائي والموصلية الكهربائية للتيار المتردد على التردد في مركبات شبكة البوليمر المتداخلة من البولي بيرول (PPy) و إيثيلين – أسيتات الفينيل (EVA) التي تم تصنيعها بواسطة أفلام EVA المشربة بكلوريد الحديديك FeCl3 التي تم غمسها في محلول بيرول,وذلك بحسابها على ترددات مختلفة تتراوح من 100 هرتز إلي 10^5 هرتز عند درجه حرارة الغرفة .

إستناداً إلى النتائج التي تم الحصول عليها فإن الملاحظة الأكثر أهمية والمثيرة للاهتمام هي أن الموصلية الكهربائية للتيار المتردد في جميع الخلطات تكون أعلى من الموصلية الكهربائية في البوليمر النقي (EVA) ؛ كما لوحظ أن الموصلية الكهربائية للتيار المتردد تظهر بشكل واضح عند الترددات العالية .

Effect of the change in PPy concentration on the dielectric properties of Poly (Ethylene–co–Vinyl Acetate) (EVA) polymer blends

Abstract

Study of the dielectric properties in interpenetrating polymer networks(IPNs) is very important because the presence of the mixing phase of PPy/EVA composite greatly influences the motion of the charge carriers in the conducting phase.

In this paper, the frequency – dependent of ε' , ε'' and σ_{ac} of interpenetrating polymer network composites of polypyrrole (PPy) and ethylene – co – vinyl acetate (EVA) synthesized by $FeCl_3$ – impregnated EVA films being dipped into solutions of pyrrole , was investigated over frequency range of 100 Hz to 10^5 Hz and at room temperature .

Based on the obtained results, it can be seen that the most important and interesting observation is that , the a.c. conductivity of all blends is higher than the pure polymer(EVA).Also observed that is ,at the high frequencies ,a.c. conductivity is appear clearly.

Introduction

Conjugated polymers have been the focus of numerous theoretical investigation in the last decades .

These systems have generated entirely new scientific concepts. Their structural versatility is attracting researchers for their multiple applications such as in batteries, light emitting diodes ,super capacitors ,biological sensors ,etc[1],[2].

They offer an unique combination of properties that make them attractive alternatives for different materials currently being used in microelectronics.

Polypyrrole   (PPy) is regarded as one of the most promising intrinsically conductive polymers for practical applications due to its relatively high electrical conductivity .environmental stability and low toxicity [3].

The typical PPy, which is insoluble and infusible ,exhibits poor process ability and lacks essential mechanical properties ,as with conventional polymers. Efforts to overcome these drawbacks have led to numerous research reports of the improved methods for both electrochemical and chemical synthesis of PPy [4],[5].

Among them ,a significant strategy to approach both high electrical conductivity and desirable mechanical properties is through the use of preparing the composites based on play and conventional polymers by different processes , such as inducing oxidative polymerization of a liquid or gaseous pyrrole on conventional polymer films or fibers [6].

De Oliveira *et al* [7] studied the dielectric characterization of conducting polymeric blends composed by conductive polypyrrole (PPy) regions formed inside a matrix of polyvinyl alcohol (PVA) containing ferric chloride ($FeCl_3$). The physical properties of the samples are dependent on the amount of

incorporated PPy as their electrical characteristics can vary from the limit of a highly insulating material to that of a very conducting polymeric film , similar in conductivity to doped electrochemically prepared PPy .

Materials used in this work

1. Ethylene Vinyl Acetate Copolymer

Vinyl acetate/ethylene copolymers . Often referred as EVA, are thermoplastic materials resulting from the Co-polymerization of ethylene and vinyl acetate (VAc).

The weight percent of vinyl acetate usually ranging from 2% to 50%. It has been reported that the amorphous content of the copolymer increases asymptotically with the VAc content.

As a representative semi-crystalline random Copolymer ,EVA is of great industrial importance .It is a typical amphoteric polymer composed of hydrophobic and hydrophilic segments and its property is expected to vary widely with the copolymers composition , for example ,the Copolymers become completely amorphous when the VAC content exceeds 50 wt%.

But EVA Copolymers are all flexible with a high flex life, have good film clarity and are resistant to water , salt and other environments .

We have used EVA with 19% vinyl acetate content , its properties given in table (1) .

Table(1) physical properties of EVA Copolymer

Property	Value
Density(g/cm^3)	0.93
Melting point(c^o)	81
Brittleness temperature (c^o)	-76
Chemical Resistance to strong alkalies	Excellent
Elongation at break(%)	600-900

2. Polypyrrole Conducting polymer

Polypyrrole (PPy) is one of the most interesting conducting polymers become it exhibits high conductivity [8] .The composites formed with low contents of PPy demonstrate reasonable high conductivities .

On the other hand ,poly ethylene –Co –vinyl acetate (EVA) is a suitable host because it is readily available , and is easy to cast into desired forms maintaining the mechanical integrity of the matrix.

There have been many applications suggested for such materials including sensors, electrochromic devices, corrosion inhibitor , electrochemical actuators , polymeric batteries, etc. This wide range of applications is possible due to the ability to change the electrical ,optical and mechanical properties of these polymers by dopant or by controlling synthesis conditions.

Some important features will be mentioned below in table(2).

Table(2) physical properties of pyrrole monomer

Property	Value
Molecular formula	C_4H_5N
Purity(%)	99%(extra pure)
Molecular weight	67.69
Density (gm/cm^3)	0.69

3. Ferric Chloride as an oxidant

Anhydrous ferric chloride symbolized as FeCl3, which is free from water is used as an oxidizing agent in the polymerization of pyrrole monomer within the matrix of EVA Copolymer.

Preparation of the composites

Interpenetrating   polymer networks (IPNs)method is used to prepare the composite films of EVA/PPy with different contents of polypyrrole.

IPNs are intimate combinations of two polymers with either both in network form or one in network form and other is a linear polymer or monomer ,at

least one of which is synthesized or cross linked in the immediate presence of the other.

Samples of EVA/PPy were prepared by taking 0.75 gm of EVA and 0.25 gm of anhydrous $FeCL_3$ and then dissolved in 20 ml of toluene.

The solution was then poured to a glass petri dish and left enough time for the solvent to evaporate and then getting the sheet.

The $FeCl_3$ impregnated EVA so formed films were then immersed in aqueous solution (10 ml) of pyrrole monomer for times ranging from 0.5 to 24 hour , the PPy content by weight percent is calculated by using the weight method during IPN process, before and after processing , the PPy content in the EVA matrix is given in weight percent as tabulated in table (3).

Table(3): composition of different samples.

Sample	Polymerization Time(hr)	PPy Content wt%
1	0.5	12%
2	2.0	15.7%
3	4.0	16.5%
4	6.0	18.8%
5	24	31%

The films were then dried and dipped in water for 72 hr to leach out all the unreacted $FeCl_3$. Then they were put in an electric oven at 60 c^o for 72 hr for further drying.

A.C. Electrical Measurements

The dielectric properties were measured using a bridge (type GM Instek LCR–821 meter) in the frequency range $10^2 - 10^5$ Hz ,and at room temperature. The samples were in circular forms of range $0.20 - 0.45$ *mm* thick and 1 *m* in diameter. The two opposite faxes of the film were coated with a thin layer of silver paste , the layer is 1 *cm* in diameter as a contact zone .Copper wires

were fixed on both surfaces, and the specimen was mounted on a sample holder.

The dielectric constant ε (real part of the dielectric constant) of the samples was calculated by using the relation:

$$\varepsilon' = \frac{d}{\varepsilon_\circ A} C$$

Where :–

C: The capacitance of the sample ,F.

d:The thickness of the sample ,m.

A:The cross–sectional contact area of the sample, m^2.

$\varepsilon_\circ$: The permittivity of free space ($\varepsilon_\circ$=8.85x10^{-12} f/m).

Results and Discussion

Recently ,scientific interest in polymers blends has intensified [9–11]. Polymer blends give the possibility to combine contrary properties of different polymeric materials , the range of behavior combinations being higher than that achieved by copolymerization. Thus, blending of polymers is an effective way of producing advanced multicomponent polymeric systems with new property profiles. From the fundamental point of view , polymer blends are interesting systems for studying polymer interactions and phase separation at microscopic levels[12].

The study of charge transport in conducting polymer composite materials is very important because the presence of matrix phase greatly influences the motion of the charge carrier in the conducting phase. Another class of polymer composite materials is represented by interpenetrating polymer networks(IPNs)[13]. IPNs are intimate combinations of two polymers with either both in network from or one in network from and the other a linear polymer, at least one of which is synthesized or crosslinked in the immediate presence of the other.

## 1- Dielectric constant and Dielectric loss of PPy /EVA Blends

We try now to study an IPNs system, that is, PPy – EVA. Dependence of dielectric constant and dielectric loss as a function of frequency ranging from $100 - 10^5$ Hz at room temperature for the pure EVA and its composites (with PPy) is plotted in Figures (1) and (2),respectively.

The inset of Figure (1) and (2) show dielectric constant ε' and loss ε'' as a function of frequency for pure EVA. In the case of EVA pure as well as the composites , ε' shows decrease from its initial higher values.

Above 10^3 Hz (for all composites except samples filled with 12% and 15.7% PPy) the dielectric constant remains nearly the same .In a similar fashion Figure (2) shows that the dielectric loss also decreases steeply as frequency increases .
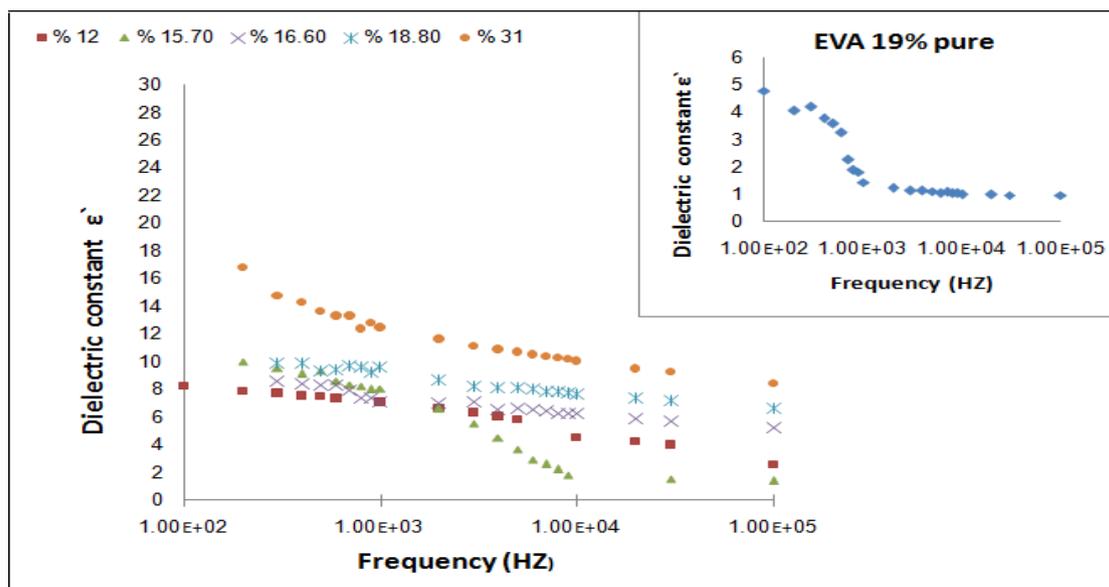
Figure(1):The frequency dependence of dielectric constant for the pure EVA and its composites (with PPy)
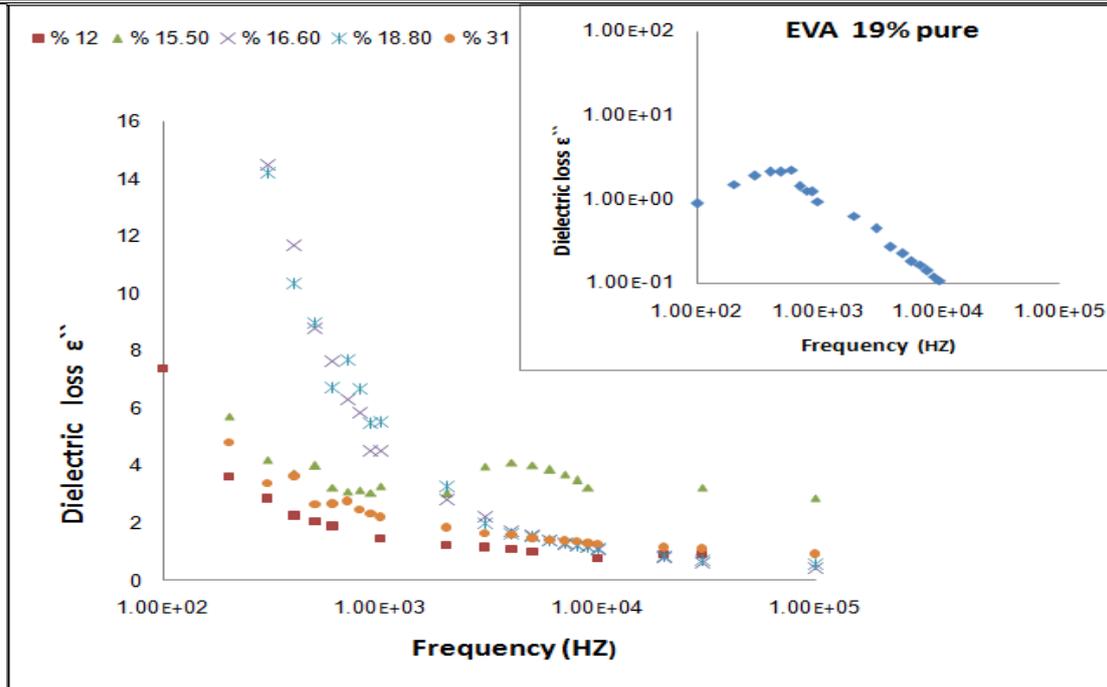
Figure(2):The frequency dependence of dielectric loss for the pure EVA and its composites (with PPy)

It can be observed that , ε' as well as ε'' values are higher for the higher content of PPy ($\leq 31\%$) in the composite (for lower frequency). At 100 Hz (and at room temperature), the dielectric constant for the composite samples with (31%) PPy is about 16. This value decrease to about 8.5 for the EVA sample loaded with (12%) PPy .On the other hand, the value of the dielectric constant for pure EVA at this frequency is about 4.

The corresponding dielectric loss for the composite samples with(31%) weight percent is about 11.5 at 100 Hz frequency . the value decrease to 3.5 for the composite with (12%)weight percent of PPy . Similarly the dielectric loss for pure EVA is about 1.5 at same frequency.

As our samples are heterogeneous ,dielectric constant may arise due to interfacial and space charge polarization at frequency from 100 Hz to 10^5 Hz. At lower frequency the dipole can respond rapidly to follow the field and dipole polarization has its maximum value , so highest dielectric constant and dielectric loss. At higher frequencies dipole polarizability will be minimum, as the field cannot induce the dipole moment, so dielectric values attain minimum[14] .

For pure EVA, dielectric constant and dielectric loss behavior may be due to the free motion of the charge carriers. In the case of composite , while PPy content is less(i,e. 12%) in the polymer interface between the polymers EVA and PPy is poor leading to decrease in conductivity and dielectric behavior.

As the PPy content is more (i.e. 31%) in the polymer blend , orderness increase, so packing density increases , interface between the polymers is more leading to maximum space charge polarization (Maxwell Wagner polarization) contributing to relatively highest dielectric constant behavior.

$2-$ A.C. Electrical Conductivity

The frequency dependent electrical conductivities of EVA/PPy blends have been presented in figure (3). The most important and interesting observation is that, the a.c conductivity of all blends is higher than the pure polymer (EVA).

For example, the bulk conductivity of pure EVA was measured to be about 5 x 10^{-9} Ω^{-1} cm^{-1} at100 Hz , whereas for (16.6%) PPY , it is 3×10^{-7} Ω^{-1} cm^{-1}. it also found that conductivity is higher for weight % of PPy ($\leq16.5\%$), in the polymer blend (at lower frequency).
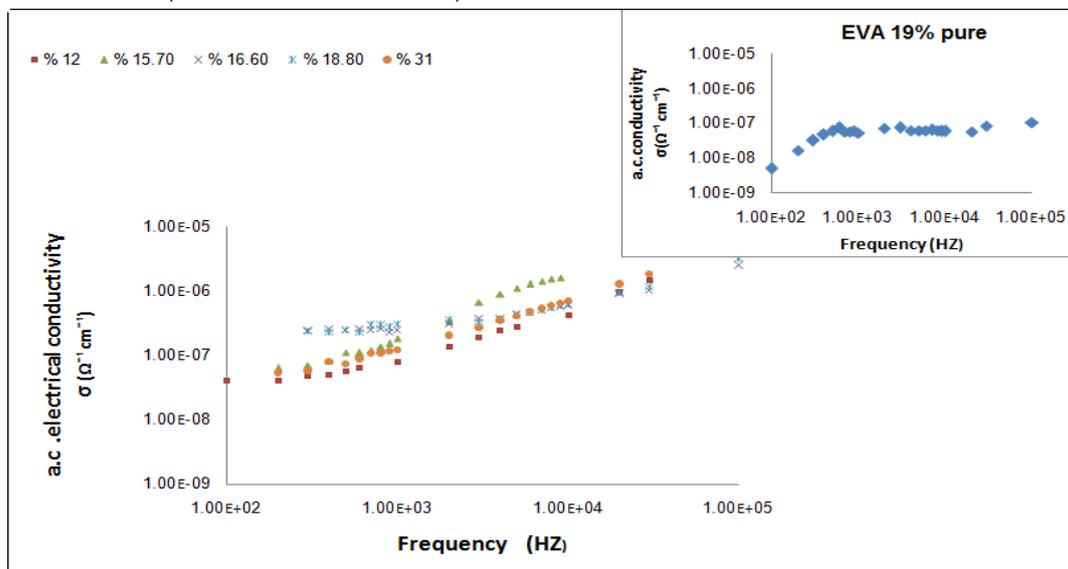
Figure(3):The frequency dependence of total conductivity for the pure EVA and its composites (with PPy)

This is evident from Figure (4),wherein , the conductivity is plotted as a function of weight percent of PPy for some selected frequencies (300, 1000, and $100,000$ Hz). Further almost all the blends show similar behavior up to

10^3 Hz, viz. that there is no much variation in the conductivity with frequency during this range.
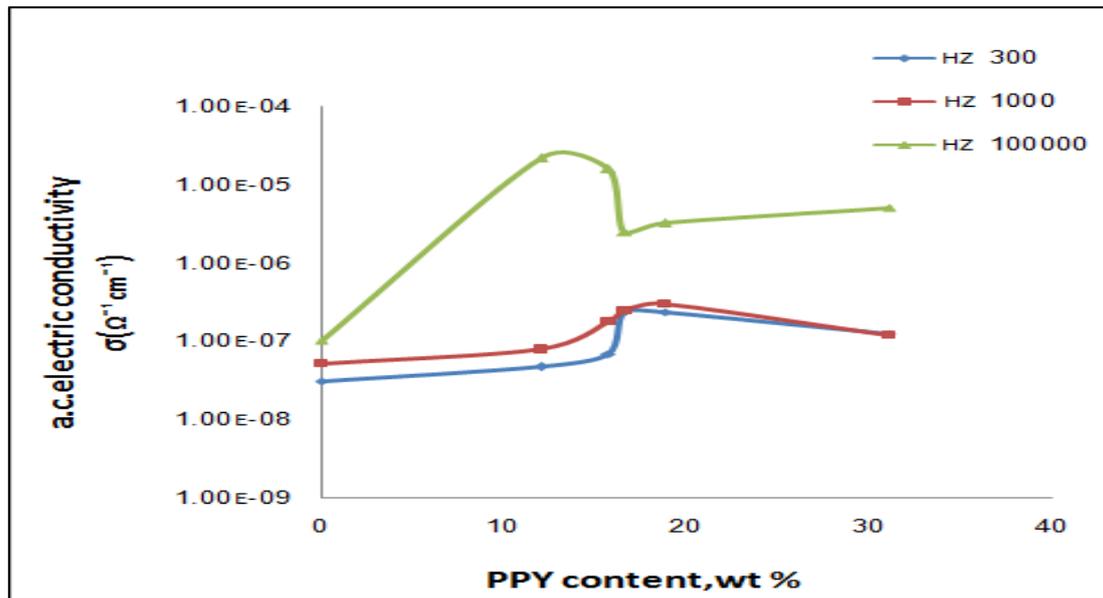
Figure(4):The dependence of total conductivity on polypyrrole content at (300,100 and 100000 Hz)

On the other hand, as the frequency is increased further ,conductivity goes on increasing and the conductivity of all blends merge together indicating the formation of excess charge carriers at higher frequencies.

Aguilar –Hernandez ,Potje – Kamloth [15] and Singh [16] accounted for the frequency dependent conductivity behavior due to two mechanisms expressed as :

$$\sigma(\omega) = \sigma_{ac} + \sigma_{dc}$$

The above equation represents the total conductivity in the context of theory of relaxation processes in dielectric materials[17],[18] which is a classical way of studying a.c. conductivity in conducting polymer.

The total measured conductivities at a given frequency is separated into $\sigma_{ac}(\omega)$ and $\sigma_{dc}(\omega)$ which is simply the limit of $\sigma_{ac}(\omega)$ when $\omega \to 0$.

Conclusion

The frequency dependence of dielectric constant, dielectric loss and conductivity of IPN composites of PPy and EVA was studied over a frequency

range of 100 Hz to 10^5 Hz at room temperature .The a.c. conductivity for specimens with PPy contents of 12%,15.7%,16.6%,18.8% and 31% is higher than the pure polymer EVA, and ,at the high frequencies ,a.c. conductivity is appear clearly .

The conductivity is independent of frequency at lower frequency .but may be dependent on temperature, so can be taken as a future work.

References :

1- Zotti,in:H.s.Nalwa(Ed),Handbook of Conductive Molecules and Polymers, vol.2, chichester ,UK, 1997, P.137.

2- R.C.Friend,N.C.Greenham,in:T.A.skotheim,R.L.Elsenbaumer,I.R.Reynolds(Eds), Handbook of Conducting Polymers, second ed ,Marcel Deker , NewYork, 1998, P.823.

3- Kuhn, H.H. Intrinsically Conducting polymers: An Emerging Technology . Kluwer ,Dordrecht , 1993 ,P.25 .

4- Wang ,H. L. and Fernandez , J.E , Macromoleeules ,1993, 26,3336.

5- Bocchi ,V. and Gardini ,G.P.J.Journal of the chemistry Society ,chemical communications , 1986,148.

6- Ojio,T.and Miyata ,S.,polymer Journal ,1986 ,18,95.

7- H.P.Deoliveira, J. material. Charact. ,vol.50,223(2003).

8- L.C.Costa .J.Euro .polym.,vol.40 ,5833 (2002).

9- H.A.Schneider and E.A.DiMarzio , polymer 33:3453-61(1992)

10- C.M.Roland and K.L.Ngai,J.Rheol,39:1691-706(1992).

11- K.Adachi ,T.Kawamoto , T. Wada ,and K.Kotaka , J.Macromolecules , 28:3588-96(1995).

12- B.B.Sauer,P.Avakian and G.M.Cohen, polymer33:2666-71(1992).

13- S.Battacharyya, S.K.saha, M.Chakravorty , B.M.Mandal ,D.Chakravory and K.Goswami ,J.Polym.sci. ,Polym.Phys.,30,1935(2001).

14-T.K.Vishnuvardhan, V.R.Kulkarni,C.Basavaraja and S.C.Raghaoendra, J.Bull.Mater.sci.,29,1,(77 -83)(2006).

15-J.Aguilar – Hernandez and K.Potje – Kamloth, J.Phys.D:Appl.Phys.34, 1700 (2001).

16- R.Singh,R.P.Tandon ,V.S.Panwar and S.Chandra, J.Appl.Phys.69, 2504,(1991).

17- K.Jonscher , Thin Solid Films, 36,1(1976).

18- A.K.Jonscher, Dielectric Relaxation in Solids (London:Chelsea Dielectric) P.86(1983).