Mechanical and Electrical Behavior of Polymer Matrix Composite and their Hybrids Reinforced with (Carbon Black–Boron) Particles

R. S. Al-Khafaji
Department of Physics, College of Education Ibn-Al- Haithem, Baghdad University, Baghdad-Iraq.

Abstract
The work is designed to study experimentally the mechanical and electrical behavior of polymer matrix composites and their hybrids which reinforced by carbon black particles with constant volume fraction (10)% and boron particles with different volume fractions (0,2,4,and 6)% which are bounded with unsaturated polyester resin. Number of mechanical tests were done, they include (hardness, Charpy impact,and bending strength), which done at room temperature in Iraq .Results of the work show that the values of hardness increased with volume fractions of boron powder ,the best values of impact strength and elasticity of modulus present at (4)% .On the other hand,dielectric constant (ἐ) decreases with increasing applied frequency, and alternating electrical conductivity($\sigma_{a.c}$) increases as the applied frequency increases up to 1MHz, While (ἐ) and ($\sigma_{a.c}$) increased as increasing of temperature.

Keywords: hybrid composite, polyester, Boron, Black carbon,hardness, Modulus, Dielectric constant, Ac conductivity.

Introduction
Polymers have received much experimental attention in an attempt to synthesize organic polymers alternative to conventional inorganic materials, due to their unique properties, such as low density, ability to form intricate shapes, versatile electric properties and low manufacturing cost [1]. The uses of composites as dielectric are becoming more popular, therefore the electrical properties of polymer matrix composites which reinforced of particles are very important. The dielectric behavior of polymer films is of considerable interest due to their applications for insulation, isolation and microelectronics [2]. The dielectric constant and the loss factors are the most convenient and sensitive methods for studying the polymer structure [3]. The electrical conductivity of insulating polymers materials can be enhanced several orders of magnitude by incorporating some conducting filler in it [4]. Due to the low cost and good electrical conductivity, carbon black(CB)-filled polymers have been widely used for several decades in many applications [5,6]. Boron element is unmatched for its combination of strength, stiffness, modulus, hardness, and density. Boron fiber use in advanced composites, for aerospace applications requiring high strength and/or stiffness, and for selective reinforcement in sporting goods. The most notable use of this fiber is the stabilizer sections of military aircraft, dorsal longeron, and the repair of metallic airframe structures. High modulus (HM) or high strength (HS) carbon/epoxy composites can match either the tensile modulus or strength of boron composites at a more economical price, but boron/epoxy composites offer twice the composite strength [7-9]. The objective of this work is to enhance the performance of structural boron /carbon/polyester hybrid composites, through studying of dielectric properties (dielectric constant, loss factor, and alternating conductivity), furthermore, studying the mechanical properties (hardness, impact, modulus) of hybrid composite of boron - carbon-polyester.

Experimental Work
Sample preparation
The matrix used in this experiment was unsaturated polyester resin of Austria produced. It is viscous liquid, transparent, pink and it is type of thermosetting Polymer. For practical purpose the catalyst Methel Ethel Keton proxide MEKP in a proportion of 2gm for each 100gm of resin according to the standard specification of manufacturing company at standard mixing time and

temperature (15min, 30˚C) in order to achieve a homogenous solution. The optimum operating conditions including mixing speed, mixing time, are investigated and found experimentally to be 500 rpm, 15 min respectively. These conditions are followed in the preparation of experiments. The rate of polymerization for this resin is too slow. Cobalt napthenate catalyst as accelerator in a proportion of 0.5 gm for 100gm of resin was used. The matrix was doped with fixed weight ratio (10)% of fine powder of black carbon supplied by Schuchardt Munchen Company, and various weight ratio (0,2,4 and 6)% of boron powder supplied by Merck Company, with high purity of 99.99% as fillers or reinforced materials. The samples were prepared using solution cast technique. Where an open mold was used to give different shapes of parts depending on test that to be carried out. The mixture was left in the mold for (24) hr at room temperature to solidify. Than the cast was placed inside an oven dryer for (6) hr at (50)˚C, this step was important to reveal completed polymerization, best coherency, and to relieve residual stresses.

Measurements

Mechanical Tests

Experiments were carried out to characterize the mechanical properties of the reinforced polyester system. The mechanical (impact, bending and hardness) tests are performed. The impact strength is determined using Charpy impact instrument AMITYVILLE INC New York. While the bending strength was achieved using German Phywe Company, three point bending tester according to ASTM D790-M86. Young modulus calculated by the followed equations [10,11]:

$E = (M/S)gL^3/48I_B$ ....(1)

Where

E = Young modulus (MPa) M/S = the slope of mass deflection curve,

g = gravitational acceleration (9.8 m/s^2)

L = length of specimen (mm)

I_B = Moment of inertia = $bd^3/12$

Where

b = width of the sample (mm)

d = thickness of the sample (mm).

The hardness was investigated using Durometer Shor D.

Electrical measurements:

The parallel capacitance(C_P) and resistance(R_P) at a frequency range (100Hz-1MHz) and within the temperature range (27-70)˚C at 1MHz, were carried out using the hP-R2c unit 4274A LCR meter (Hewlett-Packard, USA) in the range of 100 kHz–10 MHz and the Agilent 4275B LCR meter (Agilent Technologies Japan, Ltd.) in the range of 1 kHz–100 kHz .

In order to obtain a good contact for electrical measurements, the prepared samples of radius 2.5 cm have been coated with silver material (paste) on both surfaces. The silver coated samples sandwiched between the two similar electrodes governed by a screw to minimize the parasite capacitance induced by the presence of air interstices at the interfaces between the sample and the electrodes.

The prepared sample was placed in a temperature controllable isolated chamber, and the temperature was measured by thermocouple.

The electrical measurements dielectric constant (έ), dielectric dissipation factor (tanδ), dielectric loss factor (ε″) and Ac electrical conductivity ($\sigma_{a.c}$) of Polyester-carbon black–boron composites of different boron contents were obtained from followed equations [12]:

$\varepsilon' = (1/\varepsilon_o)(d/A)\,C$ ....(2)

$\varepsilon''_r = \varepsilon' \tan\delta$ ....(3)

$\sigma_{a.c} = \omega\, \varepsilon_0\, \varepsilon''_r$ ....(4)

Where ε_o is permittivity of free space, A and d are the effective cross- sectional area and thickness of the sample respectively.

In the polymer material the frequency and temperature dependent conductivity is caused by the hopping of the charge carriers in the localized state and also due to the excitation of charge carriers to upper states in the conduction band [13]. The conductivity obeys the empirical universal power law relation [14]:

$\sigma_{ac}(\omega,T) = \sigma_{dc}(\omega,T) + A\,\omega^s$ ....(5)

Here σdc represents the dc-electrical conductivity, A and s are dependent on temperature.

Results and Discussion

It is observed from Fig.(1) the values of Shore hardness are increased with increasing volume fraction of reinforced boron particles to matrix due to the boron particles have excellent hardness compared with black carbon particles [15].

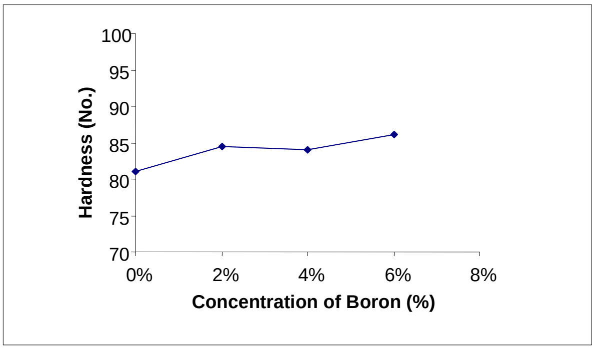

Fig.(1) Hardness versus Boron concentration of hybrid polyester composite.

The slightly decreasing of hardness at adding (4%) of boron powder to matrix may be refereed to existing of avoids which causes weakening of the chemical bond and interaction between the filler particles and matrix, Also filler particle aggregate may sometimes form a mechanically weak point [16].

In the Charpy test, the specimen is supported as a simple beam and the test is made on small notched specimen broken in flexure .The fracture energy (Uc) which is fully proportional to the impact strength (Gc).

The values of impact strength for matrix reinforced with carbon particles consider low compared with that at volume fracture (4%,6%) of boron reinforced particles as observed from Fig.(2), the reason behind these results is carbon particles have brittleness nature and the absorbed energy will decreased.

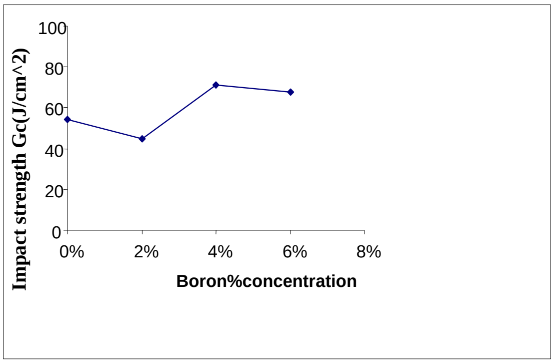

Fig.(2) Impact strength as a function of Boron concentration for hybrid polyester composite.

The best value of impact strength for volume fracture (4%) is attributed to boron reinforced particles, which absorbs part of the impact energy and undergoes deformation. The deformed domain causes shear yielding and/or formation of crazes in the surrounding matrix, which further absorbs the impact energy. Shear yielding is usually known to be the main mechanism of impact toughening [17]. The lowest value of the impact strength of the hybrid composite material consisting of (2%) boron as the reinforced particles can be attributed to the immiscibility and the poor interfacial adhesion between molecules chains of polymer (unsaturated polyester)and surface of fillers particles (black carbon and boron). Which lead to the weakening of the (cross linking) chemical bond and interaction between the matrix and filler materials.

Fig.(3) clarified the relation between mass and deflection for the samples at different volume fractions, which exhibited the linear behavior or Hookean's behavior for the hybrid composite material subjected to the applied load in the direction vertical to the surface of the sample. The ratio (deflection/mass) is represented calculated slope from Fig.(3) at different volume fractions. Modulus of elasticity of hybrids composite material increased with the difference in the particle element shape and particle size which increased the interactions among fillers. Moreover the modulus of elasticity is proportional to the size and Young's modulus of the particulate materials fillers [18].

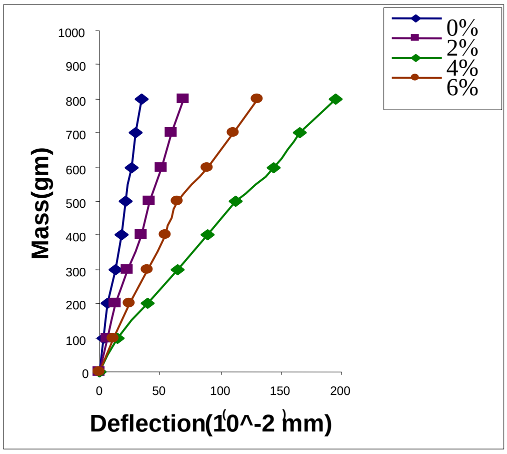

Fig.(3) The relation between mass and deflection for prepared composite with different volume fraction of Boron.

Fig.(4) was reveal Young's Modulus increased when the volume fraction of reinforcement materials increases too [19,20], this increments is obtained as a result of increasing the interactions among fillers when the volume fraction of fillers increases [21]. It is noticed that, used boron particles which have high elasticity modulus (compared with black carbon) [9, 22], increasing of its volume fraction with decreasing of volume fraction of unsaturated polyester, and the homogenous distribution of reinforced particles into the matrix which lead to restrict of polymer chains movement, and decreasing of composite material stress, consequently the value of elasticity modulus increased [23]. The decreasing in modulus of elasticity at volume fraction (6%) attributed to high viscosity of resin matrix at (modeling), which cause to poor penetration of reinforced particles into matrix material, and lead to weakening adhesion between the surfaces of matrix material and fillers particles.

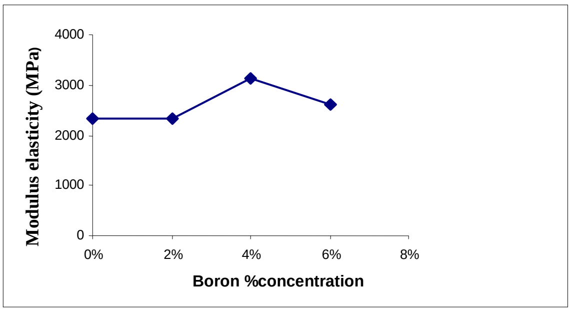

Fig.4 Modulus of elasticity against Boron concentration for prepared composite.

The dielectric constant έ of Polyester reinforced with constant volume fraction of (10%) carbon black and different volume fractions (0,2,4 and 6)% from boron as a function of applied frequency (100Hz-1MHz) was illustrated in Fig.(5). It was observed that the dielectric constant decreases with increasing applied frequency. The physics behind these result can be explained depending on the fact that, in polar materials the initial value of dielectric constant is high, but as the frequency raised the value begins to drop which could be due lack of response of the dipoles, in other word incapability of the dipole to follow the field variations at high frequency [13].

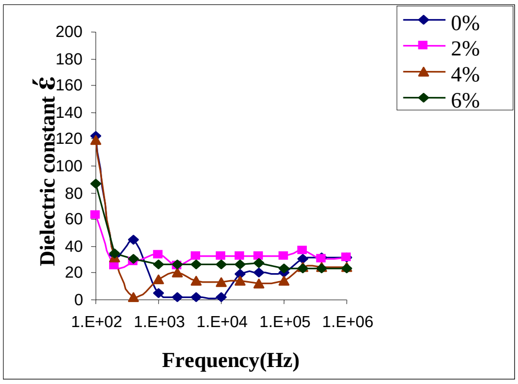

Fig.(5) Dielectric constant corresponding to applied frequency at different Boron concentration.

The resistivity of particles reinforced composites depend on the moisture content, crystalline and amorphous component present, presence of impurities, chemical composition, etc. The shapes of reinforcement determine the interparticle contact, which affect the conductivity of the system [24].

It was found that in fig.6 which referred to alternating electrical conductivity($\sigma_{a.c}$) corresponding to applied frequency at range (1KHz-1MHz), ($\sigma_{a.c}$) increases as the applied frequency increases up to 1MHz. Increasing in ($\sigma_{a.c}$) with the applied frequency attributes to the direct relation between ($\sigma_{a.c}$) and frequency as mentioned in eq. (3), and as a result of charge carriers polarization.

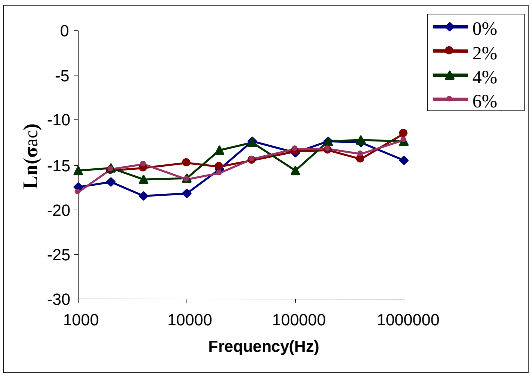

Fig.(6) Dependence of frequency on the Ac conductivity at different volume fractions of prepared samples.

The decreasing of conductivity ($\sigma_{a.c}$) for prepared composite sample without boron additive at frequency 1MHz which can be estimated from the composite material become more heterogeneous with presence of more than phase (reinforced material) which lead to increase interfacial surfaces between the matrix and the additive materials ,which that are considered to paths that allow dissipation of current from the sample. The number and length of such boundaries control uninterrupted flow of current through the sample resulting in more current and dielectric loss. On the other world, the polymeric interfaces act as charge carrier generation sites, transport and storage in polymeric system [25]. Furthermore, polyester resin have electrical resistivity higher than that of boron [22]. Experimentally Table (1) gives the obtained values of dielectric loss factor (ε″) that are measured at temperatures 27,50 and 70˚C for prepared composite samples at 1MHz frequency.

Table (1)
Loss factor ε″ versus temperature for polyester with different concentration of Boron.

Temperature (˚C)	Concentration of Boron			
	0%	2%	4%	6%
	Loss factor (ε″)			
27	0.0094	0.187	0.073	0.087
50	0.534	0.635	0.087	0.113
70	0.440	0.737	0.132	0.057

The variation of the dielectric constant έ and Ac electrical conductivity of the polyester composite with different temperatures at 1MHz frequency for (polyester –black carbon) respect to wt% of boron are plotted in Fig.(7) and Fig.(8).

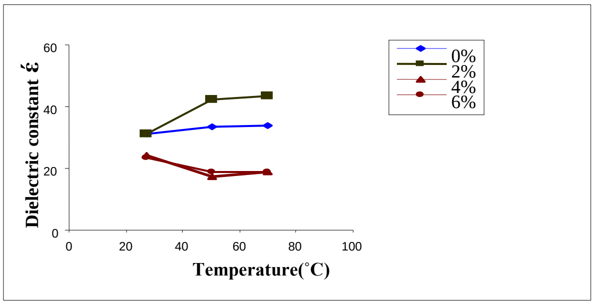

Fig.(7) Dielectric constant corresponding to different temperature of hybrid polyester reinforced with %Boron concentration.

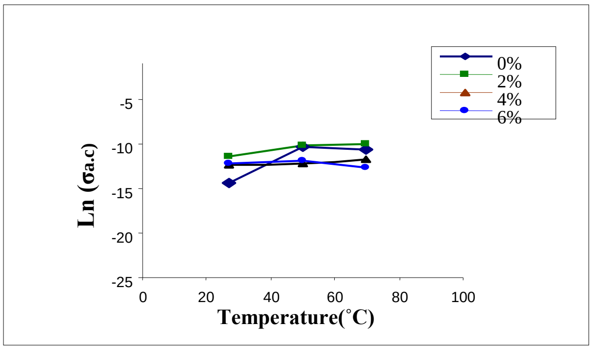

Fig.(8) Alternating electrical conductivity with different temperature of hybrid polyester reinforced with %Boron concentration.

In general, έ variation with temperature depends on the polymer types. For example in the case of nonpolar polymers the έ is independent on temperature, while for strong polar polymers the dielectric constant increases with increasing temperature. The increasing in έ with temperature, especially at higher temperature in Fig.(7), for volume fractions (o% and 2%) of reinforced boron particles can be attributed to greater freedom of the molecular chain movement at high temperature [26], which lead to increase the polarization and hence dielectric constant is increased with increase of temperature. The decreasing of dielectric constant for samples with volume fraction (4%,6%) may be referred to high viscosity of mixture which causes presence of avoids. Furthermore, from Fig.(8), nearly, it is observed the increases of conductivity ($\sigma_{a.c}$) with temperature could be attribute to that more ions gained kinetic energy via thermally activated hopping of charge carriers, as well as the increment in temperature provides an increase in free volume and segmental mobility [27]. It has been observed from Table (1). The dielectric loss factor increased with temperature for volume fraction (2, 4)%, due to chain motion of polymer is more effective due to glass transition temperature of the polymer, While the dielectric loss factor is low and remained more or less constant with increasing temperature for volume fraction (0,6)% because the orientation polarization due to chain motion of polymer can not keep phase with the rapidly oscillating electric field [28].

Conclusions

In hybrid composite material : polyester resin reinforced with hybrid particles of (black carbon –boron), the hardness increase with contain of boron, the highest values of Young's Modulus and Charpy impact appears at volume fraction 4%,The temperature and frequency dependence of dielectric constant and Ac electrical conductivity of Polyester-carbon black –boron had been carried out. The dielectric constant was found to be decrease with increasing frequency and increase with increasing temperature. This behavior was attributed to the polar nature of the polyester. The Ac electrical conductivity increases with the increment of temperature. Increasing of the values of the electrical conductivity was driven by the mobility of free charges as temperature is increased. The best values of dielectric constant and Ac conductivity observed at volume fraction 2%,we conclude that polyester –black carbon -boron composite is acceptable in electronic applications.

References

[1] El-Khodary; A.H. Oraby; and M.M. Abdelnaby; "Characterization, electrical and magnetic properties of PVA films filled withFeCl3-MnCl2 mixed fillers"; Journal of Magnetism and Magnetic Materials, 320, 1739-1746, 2008.

[2] Shekhar. S; Prasad. V; and Subramanyam. S.V; "Structural and electrical properties of composites of polymer-iron carbidenanoparticles embedded in carbon"; Materials Science and Engineering B, 133, 108-112,2006.

[3] Kindo. S;" Study on mechanical behavior of coir fiber reinforced polymer matrix composites"; M.Sc thesis, ROURKELA,2010.

[4] Chin.W.S; and Lee.G.D; "Dielectric Characteristics of E-glass-Polyester Composite Containing Conductive Carbon BlackPowder"; Journal of Composite Materials 41, 403-417, 2007.

[5]Harris.B, "Engineering composite materials", The institute of materials, London, 1999.

[6]PENG .K.Y;" The effect of carbon black and silica fillers on cure characteristics and mechanical properties of breaker compounds "; M.Sc thesis,2007.

[7]Reinhart. T.J; and Clements L.L;" Introduction to Composites"; Composites, Volume 1, Engineered Materials Handbook, ASM International, 27–34, 1987.

[8] Callister. W. D; "Material Science and Engineering An Introduction";5 th, John Wiley and Sons , 2007.

[9]"Composite materials handbook", Vol.3, 1997.

[10] Mitchell B. S; "An introduction to materials engineering and science"; JOHN WILEY & SONS, INC, 2004 .

[11] Carvill.J;"Mechanical engineers data hand book"; Elsevier Science Ltd, 1993.

[12] W.D. Kingery; H.K. Bowen, and D.R. Uhlmann, "Introduction to ceramic"; 2nd Wiley New York, 1976.

[13] Raja. V; Sharma. A.K;and Narasimha Rao. V.V.R; "Impedance spectroscopy and dielectric analysis ofPMMA-Co-P4VPNO polymerfilms"; Materials Letters, 58, 3242-3247, 2004.

[14] Reicha. F.M; Ishra. M;and Gabr. M.M; "On the physical and electrical properties of polyproenal prepared by electropolymerization technique"; J. of Phys. and Chem. of Sol, 64, 1157-1161, 2003.

[15] Free Encyclopedia , http: //www .en. wikipedia. org / wiki / .

[16] Yano.S; Iwata K.; and Kurita K.;" Physical Properties and Structure of Organic-inorganicHybrid Materials Produced by Sol-gel Process", Material Science and Engineering, C6, 2, 75-90, 1998.

[17] Gupta A. K. & Jafarri S. H., "Impact Strength and Dynamic Mechanical Properties Correlation in Elastomer-Modified Polypropylene." Journal of Applied Polymer Science, Vol. 78, John Wiley & Sons Inc, 962-971, 2000.

[18] Abdul-Hakem.A"Study the Effect of Adding the Iraqi Ceramic Raw Material (Bauxite + Kaolin) to a Thermosetting Epoxy Resin on the Mechanical Properties of Polymer"; M.Sc. Thesis, Machines & Tools Eng. Dept., University of Technology, Baghdad-Iraq,2002.

[19] Alwan. K. H; "Study the Influence of Adding Nickel Powder to a Thermosetting Epoxy Resin on the Mechanical Properties"; M.Sc. Thesis, Machines & Tools Eng. Dept., University of Technology, Baghdad-Iraq, 2002.

[20] Kinloch. A.J; and Taylor .A.C;"The Mechanical Properties and Fracture Behavior of Epoxy-Inorganic Micro- and Nano-composites"; J. of materials Science, 41, 11, 3271-3297, 2006.

[21] Takahashi.K, Ikeda.M; Harakawa.K; Tanaka.K and Sakai .T, "Analysis of the Effect of Interfacial Slippage on the Elastic Moduli of a Particle-Filled Polymer"; John Wiley and Son's Inc. Copyright, J. Poly. Sci.: Polymer Physics; 16, 3, 415-425, 1978.

[22] Shackelford .J. F. ;and Alexander .W; "Materials Science and Engineering Handbook"; CRC Press LLC, 2001 .

[23] Higgins. R. A; "Materialsfor engineering and technicas"; Elsevier Ltd, 2006.

[24] Pathania.D, and Sing h.D; " A review on electrical properties of fiber reinforced polymer composites"; International Journal of Theoretical & Applied Sciences,1,2,34-37, 2009.

[25] Tripathi. A. K., and Pillai.P.K.C, Proceeding of the 5^{th} International symposium on electrics, Heidelber, IEEE, New YorK, 1985.

[26] Akram. M; Javed. A; and Rizvi . T.Z; "Dielectric properties of industrial polymer composite materials"; T.Z, Turk J Phys., 29, 355, 2005.

[27] Harun. M.H; Kassim.E.S; Hussain.M.Y; Mustafa.I.S; and Omer .M.A;" Temperature dependence of ac electrical conductivity of PVA-PPY-FeCl3 composite polymer films"; Malaysian polymer Journal, V.13, N2, 24-31, 2008.

[28] Li.T.C; Tjong.S.C; and Li.R.K.Y;" Dielectric properties of binarypolyvinylidene fluoride/barium titanate nanocomposites and their nanographite doped hybrids"; eXPRESS Polymer Letters,5,6,526-534,2011.

الخلاصة

صمم العمل الحالي لدراسة السلوك الميكانيكي والكهربائي عملياً للمواد المركبة البوليميرية ومركباتها الهجينة (Hybrids) المدعمة (Reinforced) بحبيبات اسود الكربون بكسر حجمي ثابت ١٠% وحبيبات البورون بكسور حجميةمختلفة (٠ و ٢ و٤ و ٦)% والمترابطة براتنج البولي استر الغيرمشبع .اجريت اختبارات ميكانيكية شملت (الصلادة، متانة الصدمة، متانة الانحناء) وقد تبين ان الصلادة تزداد مع الكسر الحجمي لحبيبات البورون ، بينما افضل قيمة لمتانة الصدمة ومعامل المرونة كان عند ٤%. على الجانب الاخرنجد ان ثابت العزل يقل مع زيادة التردد المطبق في حين التوصيلية الكهربائية المتناوبة تزداد مع التردد.فضلا على ذلك بزيادة درجة الحرارة يزداد كل من ثابت العزل والتوصيلية.