Journal of Al-Nahrain University Vol.16 (4), December, 2013, pp.125-133 Science

Improvement of Mechanical Properties for Electrical Conductive Polymer Composites

Samah Mohammed Hussein
Department of Applied Science, Material Science Branch, University of Technology.

Abstract

Polyaniline (PANI) has been studied extensively as a conducting polymer because of its environmental stability. However, its applications are limited because of its poor mechanical properties. The goal of this study is to improve mechanical properties whilst still retaining electrical conductivity The method was applied for preparing the conductive PANI composites by deposition of the PANI on the prepared composites (UPE / glass fiber) and (UPE / Kevlar fiber). The chemical oxidative method was adopted for polymerization of the aniline and simultaneously protonated of PANI with a hydrochloric acid at concentration (1M). The used oxidation agent is Hexahydrate Ferric Chloride ($FeCl_3.6H_2O$). The conductivity results indicated the prepared composites lie within semiconductors region and continuous increase unless after immersed it in the preparing solution after 8weeks.The mechanical properties (bending, hardness) were studied, and also estimated as a function of water and preparing solution absorption with submersion time at room temperature for a period up to 8weeks. The obtained results showed to be increase for both properties unless after continuously immersion despite to be responded to the immersion. These results no affected on the conductivity results.

Introduction

Electrical conducting polymers have been the subject of continuous interests to the chemists, physicist, materials and device scientists for many years [1]. Although the traditional involvement of polymers in application has been as electrical insulation, dielectric in capacitor [2], electrical conducting polymer is widely desirable [3]. The conducting polymer composites are produced by combining a host of insulating polymer (namely, polycarbonate, poly (vinyl chloride), etc with any conducting materials such as a carbon or metal. These composites will have the conducting properties of the conducting material and some mechanical properties of the host insulating\.polymer [4]. A class of electrical conductive polymers that are not obtained by filler addition has been developed. These are actually conductive polymers that can be deposited from solution as, for example, homogeneous films. The degree of conductivity can be controlled by the materials and processing used [5]. Conductive polymers can have greater range of electrical conductivity than in organic semiconductors. In the last decade, considerable amount of investigations on conducting polymherterocyclic polymers have been carried out such as polypyrrole, polythiophene, oligothiophenes, polyaniline, etc. [6]. Among the conducting polymers, polyaniline (PANI) and polypyrrole (PPY) have attracted much interest worldwide because of their high environmental, thermal and chemical stability and their high electrical conductivities. The electrical conductivity of these polymers is between (10^{-5} S.cm^{-1} and 10^{2} S.cm^{-1}) while being doped, where as common insulators exhibit conductivities below 10^{-12} S.cm^{-1}, with a simple protonation process in PANI and PPY [7]. Polyaniline (PANI) can be found in one of the five distinct oxidation states leuco, emeraldine, protoemeralsine, nigraniline and Pernigraniline [8]. PANI has shown many promising applications in industries related to high technologies [9]. It sees ms to be available material for many potential uses in electric and electronic devices [10]. PANI can be used in active electrodes, rechargeable batteries, etc. [11]. However, its applications are limited by its poor mechanical properties.

Researches in the field of conductive polymers have attracted considerable attention for more than (20) years. R.V.Gregory et al. [12], in (1989) studied a process of polymerizing pyrrole and aniline on the surface of textile composites encasing each single fiber of textile assembly with a smooth, coherent layer of electrically conductive polymer and discussed some of the physical properties of the textile composites. Y. H. Park et al. [13], in (1992) synthesized highly conducting nylon-6 composites by exposing nylon-6 films or fabrics impregnated with an oxidizing agent, cupric chloride, simultaneously to aniline and hydrochloric acid vapors. R. Anbarasan et al. [14], in (2000) studied graft polymerization of polyaniline (PANI) to nylon 66 fiber that was carried out in two different media, hydrochloric acid and ρ-toluene sulphonic acid (PTSA), using peroxoydisulfate (PDS) as an initiator. S. Geetha et al. [15], in (2005) investigated a method to enhance the electronic conductivity of polyaniline grafted E -glass fabric.

Polyester/fiber composites are widely used due to combination of good physical, mechanical properties while PANI forms a group of model electrically conductive polymers. The project incorporates these materials to accomplish this goal.

Experimental Part

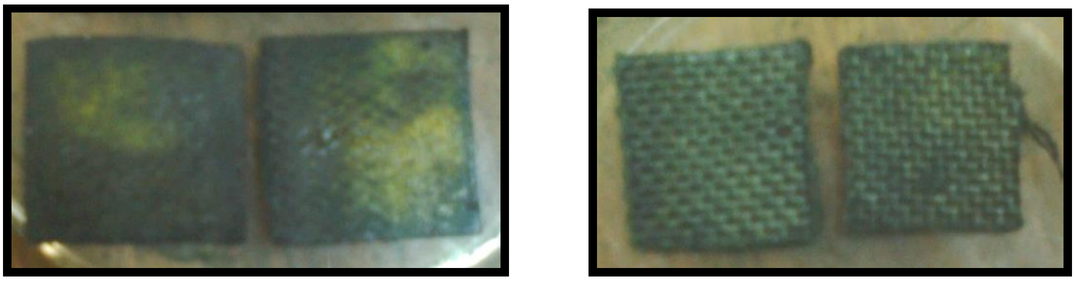
Materials:

The materials used to manufacture the composite are un saturated polyester resin (UPE), hardener, Kevlar fiber and glass fiber.UPE is thermo set polymer used as transparence liquid which transforms into a solid state after adding the hardener to it in a weighting percentage of (100:2), according to standard specificities of manufacturing company at standard mixing time and temperature (15 min, 30 °C) in order to achieve homogenous solution. In UPE low temperature curing is carried out. Curing is done with cobalt octate as accelerator and with either MEKP alone or with MEKP mixed with t-butylperbenzoate. UPE density is (1.15 gm/cm^3). The E-glass fiber and Kevlar fiber type (49) of woven roving shape were used for the reinforcement composite, with the volume fraction ratio of the fiber (ϕ = 15 %). Hand lay-up technique was used for preparing composite sample, and the testing samples were obtained by cutting the casted sheet according to related ASTM for bending test. The materials that used to obtained electrically conductive samples are monomer (Aniline) (a product of BDH chemicals Ltd pool England), hexahydrate ferric chloride ($FeCl_3.6H_2O$) (a product of BDH chemicals Ltd pool England), hydrochloric acid (HCl), 36 % of density 1.08 gm/cm^3, (supplied by BDH Company), and distilled water. The method was applied to prepare electrical conductive composites by the oxidative chemical polymerization of aniline carried out by using ($FeCl_3.6H_2O$) as an oxidant agent and protonated of PANI with hydrochloric acid.

Preparation Method of Electrically

Conductive Samples:

In this method, polyester /E-glass fibers composites and polyester/ Kevlar fibers composites were immersed in solution contains (6 ml) of aniline with (200 ml) of (1M) (HCl) acid, where put in clean glass beaker. This beaker placed in thermoster and surrounded with ice piece and the temperature was in the range (4-7 °C) for (7 day). Then we prepared solution contains (6 gm) of Hexahydrate Ferric Chloride ($FeCl_3.6H_2O$) as the oxidant agent with (100 ml) of (1M) (HCl) acid were poured on the above solution with stirring for (30min) at temperature of the range (4-7 °C) and then the samples are removed from the solution,then dried by exposed them to air for (24hr). The shape of composite samples prepared in the above method was sliced to equally pieces (2×2) cm^2. Fig.(1) illustrates the composite obtained by this method.



(a) *(b)*

Fig.(1) Image for shape composite after preparing method (a) UPE/kevlar fibers/PANI (b) UPE/glass fibers/PANI.

Measurements:

I– V Characteristic Measurements:

Studying of the I-V characteristic is essential in order to calculate the conductivity of the prepared samples. It was carried out on a two – point probe connected to a D.C power supply in the range of (0-30) voltage, supplied by Farnell. It provides an output voltage from (0-30) volt across the sample. The resulting current was measured with digital multimeter supplied by SUNS. The conductivity is calculated according to the relation (1) and (2).

V = IR Ohm's law..(1)

$$R = \frac{L}{\sigma_e A} \quad \text{...(2)}$$

Where the resistance R is proportional to the length of sample L (m) and cross-sectional area A (m^2) and conductivity σ_e ($S.cm^{-1}$).

Mechanical Measurements:

Three-point bending Test:

The modulus measures the resistance of materials to elastic deformation; the stress (σ) is related to the strain (ε) within linear elastic deformation of materials by Young's modulus (E) (Hook's law). Three-point bending test system (Phywe) is used to determine the modulus of elasticity. The distance between the supports was fixed at 80mm. The following equations are used to determine Young's modulus of the specimens [16].

$$E = \frac{Mgl^3}{48IS} \quad \text{...(3)}$$

$$I = \frac{bd^3}{12} \quad \text{...(4)}$$

Where E is Young's modulus (N/m^2), M is the mass, g is gravitational acceleration ($9.8 m/sec^2$), l is the length of the specimen, I is the moment of inertia, S is the deflection and (M/S) is the slope of linear part of the mass-deflection relation, where b and d are the width and thickness of the specimen respectively.

Hardness test:

In this test we used manual device for hardness measure is called (measurement of durability).This device (shore D) consist of spring for it apparent dibber from bore in substrate where be substrate emplaced interview for sample, and with cyclic shape Does the dibber with sample push by spring [17].Ashore hardness (scale D) instrument of model (TH210) with integrated probe standard ISO 9001 was utilized.

Immersion time effect:

The effects of immersion in (preparing solution above contains of ($FeCl_3.6H_2O$) with (1M) (HCl) acid and in distilled water on conductivity, bending and hardness measurements for composites were studied during of time (8 weeks). Specimens for conductivity, bending and hardness tests were submerged at room temperature (22 ^oC). The specimens were removed from the distilled water and the preparing solution after (7 day).

Results and Discussion

I– V Characteristic:

In general the current measurement of UPE/ Kevlar fibers / PANI composites that prepared in our method gave higher data than the UPE/ glass fibers/ PANI composites prepared in the same method. We can notice that the current increased gradually with the applied voltage range for these composite where the high value of current obtained (in the 8 weeks) for UPE / Kevlar fibers / PANI composite is (16.95 m Amp) and UPE / glass fibers / PANI composite is (11.27 m Amp) at the applied voltage (30 volt). As shown from Fig.(2) that shows the variation of the current as a function of the applied voltage for the UPE/ Kevlar fibers /PANI and UPE/ glass fibers /PANI composites that immersed in (HCl (1 M) $FeCl_3.6H_2O$) and from Fig. (2) to (10), we can notice the current increased quickly with the applied voltage range for the both composite after (8 weeks). When ohmic law is followed, there is a linear relationship between I &V, if there is no charge carrier trapping and no hindrance to current transport between electrodes. In general the I-V characteristic of the most composites shows a linear relationship indicating that power dissipation was negligible within the composites [18, 19].

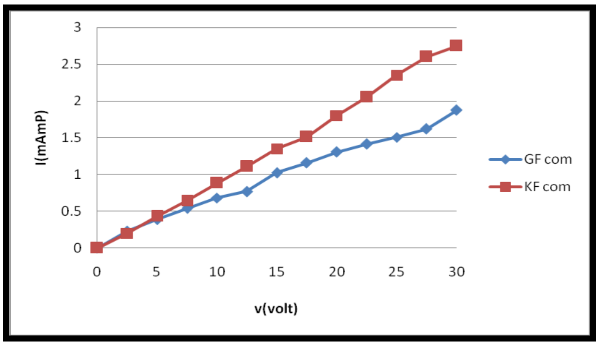


Fig. (2) I-V characteristic of the UPE/glass fibers/PANI (GF com) and UPE/Kevlar fibers/ PANI (KF com) composites.

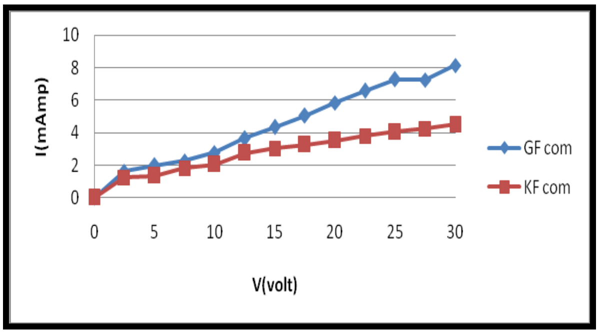


Fig. (3) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (1 week).

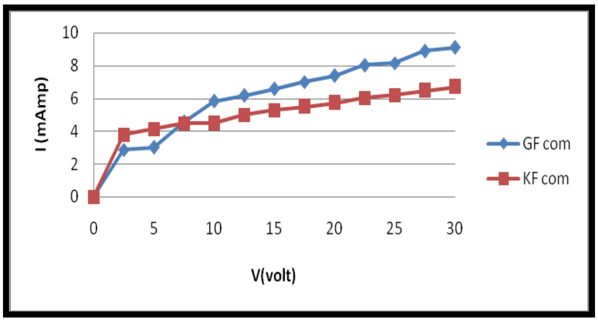


Fig. (4) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (2 weeks).

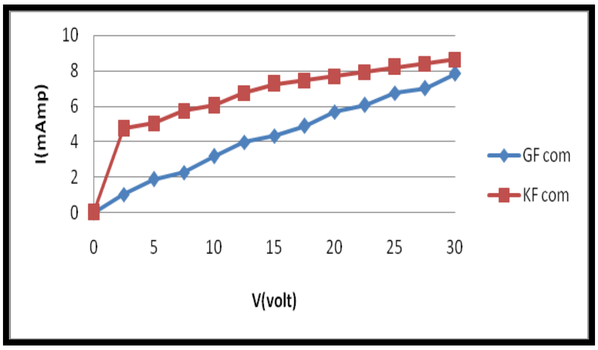


Fig. (5) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (3 weeks).

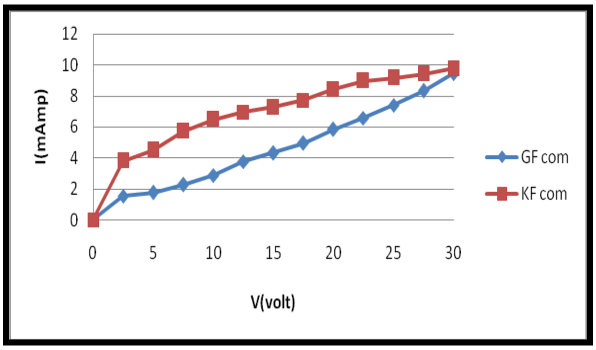


Fig. (6) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (4 weeks).

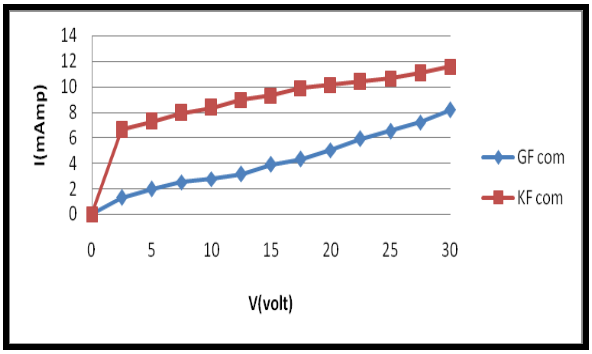


Fig. (7) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (5 weeks).

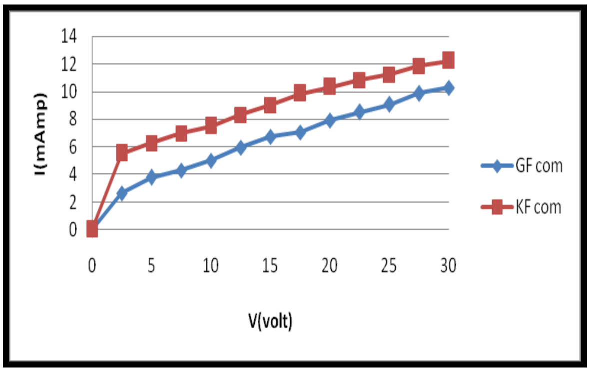


Fig. (8) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (6 weeks).

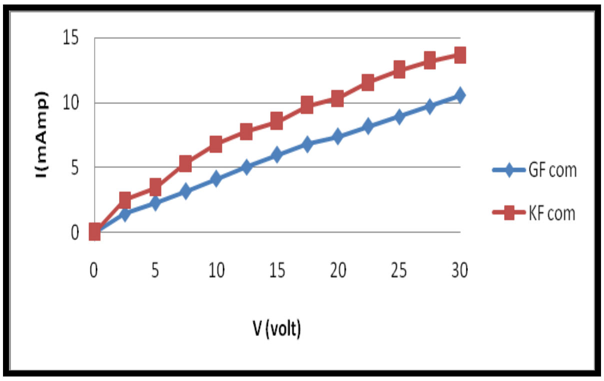


Fig. (9) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (7 weeks).

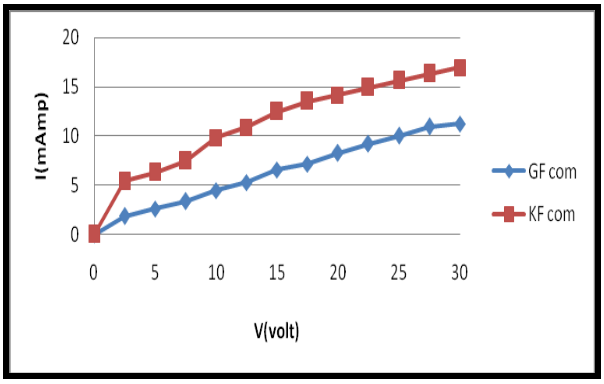


Fig. (10) I-V characteristic of the UPE/ glass fibers / PANI (GF com) and UPE/ Kevlar fibers /PANI (KF com) composites after (8 weeks).

Conductivity as a Function of Time:

From I-V characteristic figures we can obtain the value of the electrical conductivity from the reciprocal slope (R) and applying it in equation (2). Generally UPE / Kevlar fibers / PANI composite have higher value of Conductivity (249.46×10^{-3} $S.cm^{-1}$) from the UPE/ glass fibers/PANI composites (186.13×10^{-3} $S.cm^{-1}$) within increasing the immersion time and we can notice after (8 week) the conductivity reached to higher value for both composites but the UPE/Kevlar fiber / PANI composites have higher value for the all weeks until before increasing the immersion. This case belongs to increasing coating of polyaniline completely on the surface of the samples and hence the calculated conductivity represents the intrinsic conductivity of the composites [19]. A Fig.(11) shows change of conductivity values with the immersion time. These values for conductivity for (UPE / Kevlar and glass fibers / PANI composites) are within semiconductors range. Table (1) represented the conductivity value for all samples for all the weeks where the conductivity of the prepared composites lies in the semiconductors region as a whole because the conductivity of semiconductors lies between (10^{-6}–10^{5}) ($S.cm^{-1}$) [20].

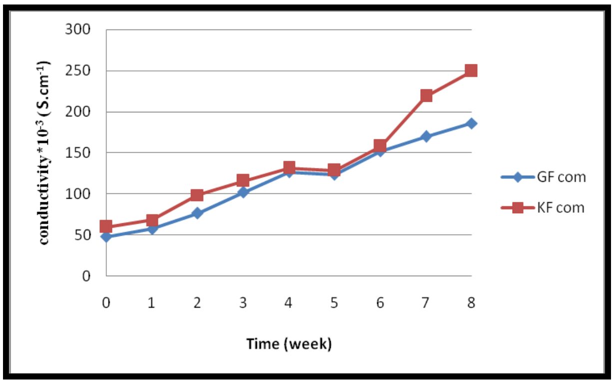


Fig. (11) change of conductivity values with time of the UPE / glass and Kevlar fibers/PANI composites before and after immersion in (HCL (1 M) and $FeCl_3.6H_2O$).

Table (1)
Shows the conductivity values with the time for the two composites before and after immersion in (HCl) (1 M) $FeCl_3.6H_2O$).

Time (week)	*Conductivity ×10^{-3} ($S.cm^{-1}$) GFcom*	*Conductivity ×10^{-3} ($S.cm^{-1}$) KFcom*
br imm	48.204	59.86
1	57.483	68.165
2	76.29	98.43
3	102.13	115.75
4	126.43	131.47
5	123.65	128.66
6	152.08	157.91
7	169.85	219.08
8	186.13	249.46

Bending Test:

The test results for bending property of the UPE/ glass fibers /PANI and UPE/ Kevlar fibers /PANI composites presented from Fig. (12) to (15), which shows the effect of load on deflection of the samples. The Young's modulus which is used as an indication of a material's stiffness in static bending condition can be derived from the tangential slope of the load-displacement curve and calculated according to the relation

(3). From the young's modulus testing for composites demonstrated linear behavior. There are many factors affecting the modulus of the composite. The factors are the intrinsic properties of the materials or fillers, modulus, the bonding force between the matrix and fillers that is responsible for the efficiency of load transfer in the composites, filler distribution, aspect ratio and orientation of the fibers in the composite, particle size of particulate fillers, and filler content [21].

The obtained result indicates the increasing in modulus value as compared with virgin polyester. The fibrous composites, applying load on them will distribute the resulting stresses on the matrix and the fibers, which bear the highest ratio of these stresses. For this reason they have the highest Young's modulus [22]. We can notice after the immersion of samples (UPE / glass fibers /PANI and UPE / Kevlar fibers /PANI composites) in distilled water and the preparing solution contains of ($FeCl_3.6H_2O$) with (1M) (HCl) acid for long time reduces the values of young's modulus, where the chemical treatment is conducted to improve the separation of individual fibers and the adhesion with composite matrix, undesirable effects such as loss of mechanical performances, destructuration through strong swelling or surface degradation can occur [23]. One of the functions of polymeric matrix in a fiber composite is to protect the fibers from the chemical attack through corrosive environments [24]. These results shown in Fig.(16, 17) that shown the variation of young's modulus with the immersion time.

We can also notice the UPE / Kevlar fibers composites immersed in distilled water less deflection than of UPE / glass fibers composites but the deflection value decrease at continuously immersion in distilled water and the preparing time because of diffusion effect. Hence the immersion in the preparing solution not affected on the results of the young's modulus compared with the immersion in distilled water.

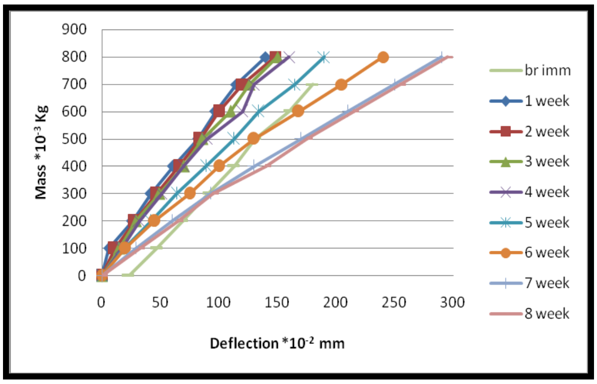


Fig. (12) Relationship between mass and deflection for UPE / glass fiber/PANI composites before and after immersion in distilled water.

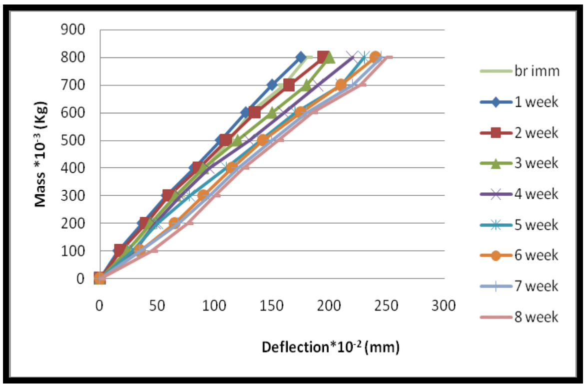


Fig. (13) Relationship between mass and deflection for UPE / Kevlar fibers/PANI composites before and after immersion in solution (HCl (1 M) $FeCl_3.6H_2O$).

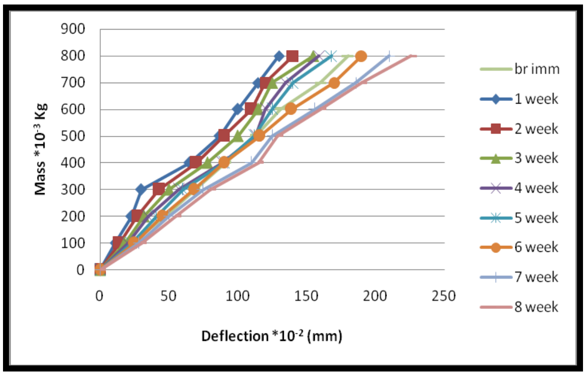


Fig. (14) Relationship between mass and deflection for UPE/ Kevlar fibers/PANI composites before and after immersion in distilled water.

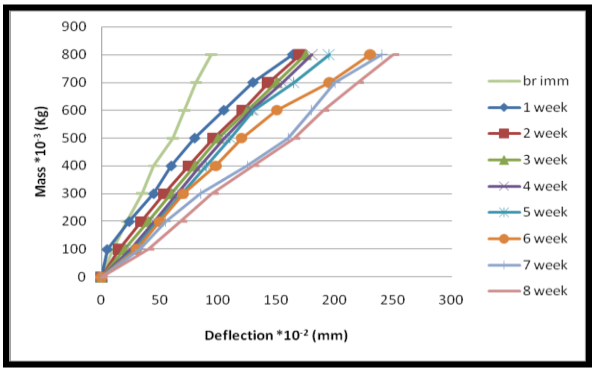


Fig. (15) Relationship between mass and deflection for UPE/ glass fibers/PANI composites before and after immersion in solution (HCl (1 M) $FeCl_3.6H_2O$).

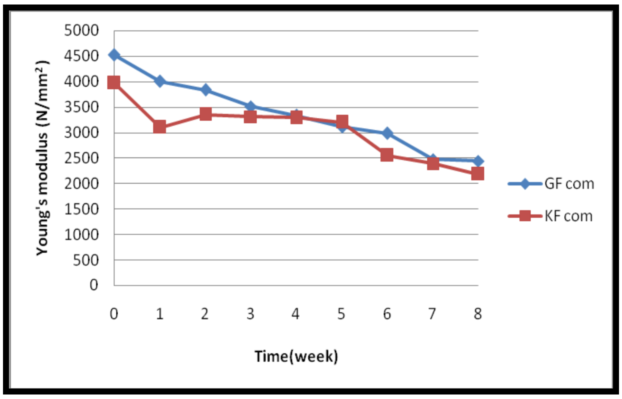


Fig. (16) The young's modulus values for UPE / glass fibers and UPE / Kevlar fibers/PANI composites before and after immersion in distilled water.

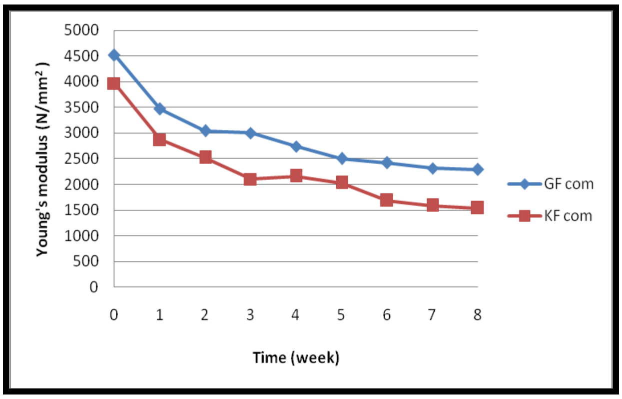


Fig. (17) The young's modulus values for UPE / glass fibers and UPE / Kevlar fibers/PANI composites before and after immersion in. solution (HCl (1 M) $FeCl_3.6H_2O$).

Hardness Test:

The measured hardness values of composite are presented in Fig. (18, 19). The hardness of samples (UPE/ glass fibers / PANI and UPE/ Kevlar fibers / PANI composites) is higher than virgin polyester. This must be expected because as filler get into the matrix the loading stress is shared by fibers resulting more rigid. It should be mentioned that surface hardness depends also on the bonding at the matrix and fibers interface, and the distribution of fibers within the matrix. This result may be explained that both forms of filler were contributed to hardness the composite, since movement of the matrix is restrained in the vicinity of each fibers, and the stress is spread through distributed fibers thus enhanced composite hardness. The emersion in distilled water and preparing solution appear decreasing not clear in the first weeks, but at the eight week the decreasing in hardness values become clear. Generally, chemical solutions play a major role in decreasing values of hardness. As the time of immersion increases, chemicals solutions work on degrading the material leading to its failure. Diffusion of chemical solutions through the materials (polymeric materials) led to break bonds with the appearance of bubbles [25]. Moreover, weak bonding between the filler and the matrix increases the porosity and hence the absorption [26].

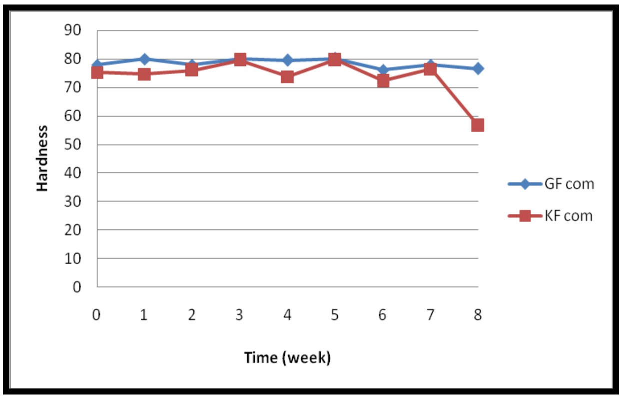


Fig. (18) The Hardness value of (UPE/ glass fibers/PANI and UPE / Kevlar fibers / PANI composites before and after immersion in distilled water.

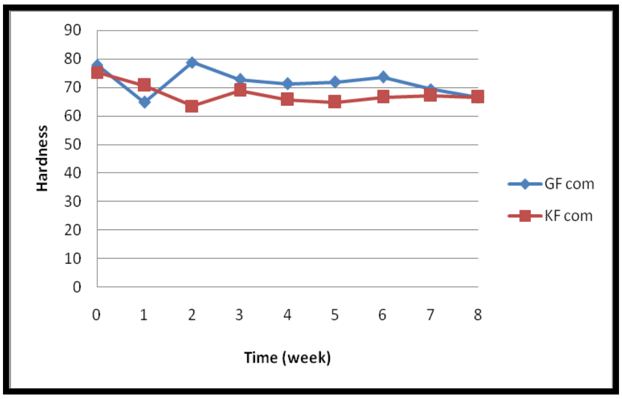


Fig. (19) The Hardness value of (UPE/ glass fibers/PANI and UPE / Kevlar fibers /PANI composites before and after immersion in solution (HCl (1 M) $FeCl_3.6H_2O$).

Conclusion

- The applied composites ((UPE / glass fibers /PANI and UPE / Kevlar fibers /PANI composites) are successful for obtaining electrical conducting composites.
- The conductivity of the prepared composites lies in the semiconductors region as a whole.
- The highest electrical conductivity is obtained for the UPE / Kevlar fibers / PANI composites.
- The continuously immersion in the prepared solution increasing the electrical conductivity for all samples.
- From the bending and hardness test, it was found that both the composites have high value of young's modulus and hardness unless after the immersion in distilled water and the prepared solution.
- The obtained results represented the ability of synthesizing electrical conducting polymer composites with high mechanical properties.

References

[1] Ajayi J. D. and Hepburn C., "Plastics and Rubber Processing and Application", Vol. (1), No.(4), 1981.

[2] Yepifano V C. I., Moma Yu. A, "Introduction to Solid State Electronics", Mir Publishers, Moscow, Chap. (1),. 1989.

[3] Al-Delaimi M. N. J., Ph.D. Thesis, "The effects of Ni, Cu, and CB Additives on the electrical, Optical, and Mechanical Properties of PMMA", Univ. Techno., Iraq, 1996.

[4] Ekramul Mohmud H. N. M., Kassim A., Zainal Z. and Yunus W. M. M., J. Science Asia, Vol. (31), P.P. 313 – 317, 2005.

[5] Monistuer T. T., "Encyclopedia of Polymer Science and Technology", John Wiley and Sons, Inc, U.S.A, Vol. (5), 1966.

[6] Aldrich, Chemfiles, Organic Semiconductors for advanced Electronics, Vol. (4), No. (6), 2003.

[7] Cao Y., Smith P. and Heeger A. J., Synth. Met., Vol. 55-57, P.P.3514-3519, 1993.

[8] LIU. L. M., Levon. K., J. Appl. Polym. Sci., Vol. (73), No.(14), P.P.2849-2858, Sep., 29, 1999.

[9] Liu, W. J., Gao G., J. Appl. Polym. Sci., Vol. (93), P.P. (956), 2004.

[10] Matsunaga T, Daifuku. H, Nakajima T, and Kawagoe T, Polym. Adv. Techno., Vol.(1), P.P.(33), 1990.

[11] Sahin. Y, Percin.S, Sahin M, and Ozkan G,Appl. Polym. Sci. Vol. (90), P.P.2460-2468, 2003.

[12] Gregory R. V., Kimbrell W. C. and Kuhn H. H., Synth. Met., Vol. (28), No.(1&2), P.P.823-835, 30 January, 1989.

[13] Park Y. H., Choi S. H., Song S. K. and Miyata S., J. Appl. Polym. Sci., Vol.(45), P.P.843-851, 1992.

[14] Anbarasan. R., Muthumani. N., Vasudevan T., Gopalan. A. and. Wen T. G., J. Appl. Polym. Sci, Vol.(79), P.P.1283-1296, 2001.

[15] Geetha S., Kumar K. K. S. and Trivedi D. Ch., J. Appl. Polym. Sci., Vol.(96), P.P. 2316-2323, 2005.

[16] Khurmi R. S. and Sedha. R. S. "Materials Science" S. Chand & Company LTD. India, 2008.

[17] Diarmid. M., A. G. "Angew. Chem Int. Ed. Engl", Vol.(40), P.P.(2581), 2001.

[18] Baht M. V. and Sundaresan E., J. Appl. Polym. Sci., Vol.(12), P.P.1615-1622, 1991.

[19] Rustum S. S., M.Sc. Thesis, "Preparation of Electrical Conducting Polymer Composites and Studying it Electrical Properties", Univ. Techno., Iraq, 2005.

[20] Bolton W., "Engineering Materials Technology", 3rd ed., (Butter Worth-Heinemann), Oxford, 1998.

[21] Mohamed Yusoff M. Z., Sapuan Salit M., and Ismail N., and Wirawan R., Mechanical Properties of Short Random Oil Palm Fibre Reinforced Epoxy Composites, Sains Malaysiana, P.P.87-92, 2010.

[22] William D. and Callister Jr.. "Materials science and engineering.An introduction", John Wiley and Sons, Inc.U.S.A., 2000

[23] Cristophe B., Frederic B., Yves G., Olivier S., "Influence of chemical treatments on surface properties and adhesion of flax fiber-polyester resin", Univ.de Bretagne sud, France, 2005.

[24] Bledzki A., Paude R. S., Ehrenstein G. W., "Corrosion phenomena in glass fibers and glass fibers reinforced thermosetting resins" Composite science and technology Vol.23, No.4, P.P.263-285, 1985.

[25] Al-Azzawi A., M.Sc. Thesis, "Study of mechanical and thermal behavior for a hybrid composite material" Univ. Techno. Iraq, 2002.

[26] Parmjit S., Anuppama, K. and Kirandeep, Journal of reinforced plastics and composites, "Mechanical and transport properties of colloidal Silica-Unsaturated polyester composites" Punjab. Univ., India, 2005.

الخلاصة

إن دراسة بوليمرالبولي انيلين (PANI) واسعة جدا وخصوصا كموصل كهربائي بسبب استقرارية خواصه للظروف البيئية المختلفة وعلى اية حال تطبيقاتة محدودة بسبب ضعف خواصة الميكانيكية. ان الهدف من هذة الدراسة هو لتحسين خصائصة الميكانيكية مع الاحتفاظ بموصلية كهربائية جيدة. ولهذا تم تحضير متراكبات البولي انيلين الموصلة كهربائياً بترسيب البولي انيلين على المتراكبات (بولي استر/ الياف الزجاج) ومتراكبات (بولي استر/ الياف الكفلر). و تم أستخدام طريقة الاكسدة الكيميائية لآلية البلمرة للانيلين وبأدخال البروتون آنياً للبولي انيلين بأستخدام حامض الهيدروكلوريك بتركيز (1 مولارتي) وبأستخدام العامل المساعد ($FeCl_3.6H_2O$). وقد اظهرت نتائج التوصيلية الكهربائية بأن المتراكبات البوليمرية المحضرة تقع ضمن منطقة أشباه الموصلات وتزدادحتى بعد زيادة الغمر في المحلول المحضر لمدة 8 أسابيع .وتم دراسة الخصائص الميكانيكية والتي تضمنت كل من (الإنحناء والصلادة) وقد قيست كدالة لامتصاص الماء والمحلول المحضر مع زمن الغمر لمدة 8 أسابيع عند درجة حرارة الغرفة. وقد اظهرت النتائج ان هنالك زيادة لكلا الخاصيتين حتى بعد استمرار الغمر على الرغم من انها تستجيب للغمر وهذه النتيجة لم تؤثر على نتائج التوصيلية.