

Studying Some Electrical and Mechanical Properties of Epoxy- Polyaniline (PANI) Composites

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Abstract

As ordinary known the ability of synthesizing electrical conducting polymer composite is possible but with poor mechanical properties, for the solution of this problem, we carried out this study in order to obtain both properties.

The PANI composite was prepared by using the prepared (EP/glass fiber) composite as substrate for the deposition of the PANI. The chemical oxidative method was adopted for polymerization of the aniline and simultaneously protonated of PANI with a hydrochloric acid at a concentration of (1M). The oxidation agent ($FeCl_3 \cdot 6H_2O$) was used. The conductivity results showed that the prepared composite lies within semiconductors region ($1.7 \times 10^{-3} (S \cdot cm^{-1})$). The Hall Effect measurement showed a p-type behavior for the prepared composite.

The creep and tensile behavior was studied and concluded that PANI Precipitated on the EP/glass fiber composite has no remarkable effect on the mechanical creep and tensile behavior as compared with the untreated composites with PANI. But have higher creep resistance and ultimate strength.

دراسة بعض الخواص الكهربائية و الميكانيكية لمتراكبات إيبوكسي - بولي أنيلين الخلاصة

من المتعارف عليه إمكانية تصنيع متراكبات بوليمرية موصلة كهربائياً ولكن بخصائص ميكانيكية ضعيفة ولحل هذه المشكلة تم اللجوء لهذا البحث لمحاولة الحصول على الخاصيتين معاً

تم تحضير متراكب بولي أنيلين باستخدام متراكب (الايوكسي/الياف الزجاج) كقاعدة لترسيب البولي أنيلين. تم استخدام طريقة الأكسدة الكيميائية لآلية البلمرة للانيلين وبإدخال البروتون أنياً للبولي أنيلين باستخدام حامض الهيدروكلوريك بتركيز (1M) وبأستخدام ($FeCl_3 \cdot 6H_2O$) كعامل مؤكسد. وقد أظهرت نتائج التوصيلية الكهربائية بأن المتراكب البوليمري المحضر يقع ضمن منطقة أشباه الموصلات ($1.7 \times 10^{-3} (S \cdot cm^{-1})$). أن قياسات تأثير هول بينت ان سلوكية المتراكب المحضرانها من نوع (p-type). وقد تم دراسة سلوكية الزحف وسلوكية الشد و أظهرت النتائج ان ترسيب البولي أنيلين على المتراكب (الايوكسي /الياف زجاج) ليس له تأثير على سلوكية الزحف والشد الميكانيكية مقارنة مع المتراكب الغير معامل مع البولي أنيلين ولكن أظهرت مقاومة زحف اعلى وممانعة شد اعلى .

Introduction

One of the principle characteristics of materials is their ability to conduct electrical currents. Indeed, materials

are classified by this property into conductors, semiconductors and insulators. The range of electrical conductivity observed in materials covers a range of 25 orders of

variation in any materials property while one tends to regard polymers primarily as insulators but in the past decade the discovery of highly conducting graphite intercalation compounds, metallic polysulfar nitrogen and doped polyacetylenes that can be made to exhibit metallic conductivity as well as n-type or p-type semi conductivity. This means that the range of conductivity of carbon-based polymers can be regarded as covering as similar span [1].

Much research efforts have been generated to produce composites or blends of conducting polymer film with some insulating polymers in order to overcome the drawbacks such as poor processability and lack of essential mechanical exhibit by these polymers [2].

Electrical Conducting polymer Composites:

Electrical conducting polymer composites have been the subject of continuous interests to chemists.

The conductive composites obtained are of interest in various applications such as fabricating antistatic materials, heating panels, shielding coat, anticorona layers in high voltage cables, and pressure transducers. The list is not exhaustive and new applications are still being discovered [6].

Electrical Conducting Polymers:

In general, polymers are poor electrical conductors and some polymers such as Teflon are used as electrical insulators[7].Although the traditional involvement of polymers in application has been as electrical insulation, dielectric in capacitor, electroluminescent indicators [8], a conducting polymer is widely desirable[9].

physicists , materials and device scientists for many years [3]. This interest arises from the idea of being able to combine in a single material the electrical properties of metal (high conductivity) or semiconductor (moderate conductivity) with those of polymer (mechanical strength, flexibility, light weight , low preparation ,fabrication cost, high strength –to-weight ratio, low fabrication temperature, etc.) for instance [4,5].These conducting composite or blends produced by combining a host of insulating polymers (namely, poly(styrene sulphonate), poly carbonate, poly (vinyl chloride), nitrile rubber,etc.), with any conducting polymer (such as polypyrrole, polyaniline, polythiophene etc.) in an aqueous or organic medium. These composites will have the conducting properties of the conducting polymer and some mechanical properties of the host insulating polymer [2].

A class of electrical conductive polymers that are not obtained by filler addition has recently 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 [4]. Conductive polymers can have greater range of electrical conductivity than inorganic semiconductors. Conducting polymer structures range in complexity from the simplest polymer known, polyacetylene, to heteroaromatic polymers such as polyaniline [5].

Polyaniline:

Polyaniline (PANI) is a conducting polymer of the semi -flexible rod

polymer family. It was discovered in (1934) as aniline black. It also exists naturally as a part of a mixed copolymer with polyacetylene and polypyrrole in some melanins. It is polymerized from the aniline monomer

Polyaniline can be found in one of the five distinct oxidation states [10]:

- Leuco emeraldine.
- Protoemeraldine.
- Emeraldine.
- Nigraniline.
- Pernigraniline.

The chemical structure of polyaniline illustrate is in figure (1).

Polyaniline is one of the most important conducting polymers because of relatively low cost, successful combination of chemical and physical properties, simple synthesis, good environmental stability, and adequate level of electrical conductivity [11].

Experimental part

The Experimental part includes two steps:

1- Preparation of Epoxy Composites

To improve the properties of Epoxy resins (type Conbextra EP10), they are reinforced by E-glass fabrics. the composite was prepared with the same volume fraction ratio of the fiber ($\Phi=20\%$).

Epoxy and hardener (3:1) were mixed in a container and stirred well for (3-5) minutes and composite was prepared according to the following procedure:

1. Clean galvanized metal mould with dimensions (250*250*30) mm was used for casting the sheets of the composites figure

2. Polymer sheet (fablone) was fixed on the inner mould faces before casting to facilitate the relasing of casting composites and having smooth faces.

3. Adding the fabrics, were cut and aligned in the mould, before pouring the blend. Depending on the required composite thickness, in our work, we used three layers from the fabric, were stacked until the desired thickness was obtained .Thickness of sample is about (2-2.5) mm.

4. Covering plate, with identical dimension of the mould face, was used to apply appropriate load on the casting sheet for releasing voids, bubbles, to have a specified thickness and smooth face. And then casting sheet was left inside the mould at room temperature for about (24hr).

5. After solidification, the casting sheet was released from the mould and placed in an oven at (55 °C setting temperature) for (3 hr) to post cure the considered sheets.

6. The testing samples (EP/glass fiber and EP/glassfiber/PANI composites) were obtained by cutting the casted sheet according to related (ASTM) for creep and tensile measurements.

All properties were measured at room temperature (26-28 °C). Identical procedure was used for preparing composite sample (hand lay- up technique).

Preparation methods of electrically conductive samples:

In this section, we will show the method to prepare electrical conductive composites by the

oxidative chemical polymerization of aniline carried out by using (FeCl₃.6H₂O) as an oxidant agent and protonted of polyaniline (PANI) with a hydrochloric acid.

Epoxy/E-glass fiber composite was immersed in monomer aniline for (7days). It was put in clean glass beaker at room temperature and then it removed, and directly immersed into a beaker containing acidic solution of the oxidant agent Hexahydrate Ferric Chloride (FeCl₃.6H₂O) of concentration $(20\% \frac{w}{v})$ by using a hydrochloric acid (HCl) of (1M).

This beaker was placed in a thermoster and surrounded with ice piece and the temperature was in the range of (4-7°C) for (24hr). This step is the chemical polymerization of the aniline and then the sample was removed from the solution and dried by exposing it to air for (24hr). Figure (2) illustrates the obtained composite and the morphology of the Epoxy / glass fiber composite before and after treatment with PANI as illustrated in figure(3).

Electrical Measurements:

1- (I-V) characteristic Measurements

Studying 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 on the sample connected to a D.C power supply in the range of (0-30) voltage, supplied by Farnell.

physical engineer from Al – Tehade company which consist of two coils of N₁=N₂=400 turns and I_{max} =4.5A with two poles of (2.5 cm) in

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 Ohm's law relating the current I (or time rate of charge passage) (Ampere) to applied voltage (Volt)

$$V=IR \quad \text{Ohm's law} \quad \dots (1)$$

Where R is the resistance of material through which the current is passing. The value of R is influenced by specimen configuration, and for many materials it is independent of current.

The resistance of material depends on a property called resistivity (r),; the inverse of resistively is called conductivity (S).The resistance is proportional to the length of the sample L (m) and inversely proportional to its Cross-sectional area A (m²) and conductivityS :

$$R = \frac{L}{S A} \quad \dots (2)$$

A schematic diagram for I-V Characteristic system is shown in figure (3).

2-Hall Effect:

Hall Effect is studied in order to identify the sign, concentration and mobilities (μ) of the charge carriers Hall Effect system fabricated by physical engineer from Al – Tehade Company.

A D.C. power supply in the range of (0-30) volt with current of (20A), connected to electromagnetic magnets system fabricated by diameter and the gap between poles (2cm) with magnetic field (1.591 Tesla).

Mechanical measurements

in the current (2.5A).
 The concentrations (n) and mobilities (μ) of the charge carriers in the sample was calculated from the formulas in equations (3), (4) and (5)

$$R_H = 1/e n \quad \dots (3)$$

Hence

$$R_H = V_H W / B I \quad \dots (4)$$

and

$$S_e = m / R_H \quad \dots (5)$$

Creep Behavior test

The loaded sample was under constant load with increasing time. The creep equipment model (SM106MK2TQ) was used to test samples under constant stress.

After fixing the sample in situ, the required stress was applied (20 N); ΔL was determined by the dial gauge (0.01) against the recorder time. It is possible to find out the relation of strain – time (e – t) by dividing ΔL by the original length of the sample. To make the applied stress constant for our specimen, the following equation is used [12];

$$S_* = p / A = \frac{(2.96 + 8 m) * 9.81}{A} \quad \dots (6)$$

The amount (2.96) represents specific constant for the instrument of creep. Where P is: the amount of applied force to the sample (N).

m is: the sum of the used masses (Kg), which represents the masses of the beam+hanger+Supporting pin that belong to the instrument in addition to hanged mass. A is: The cross sectional area of the sample (m²).

The used value of the applied load on the polymer composite samples was around (20) N.

The creep rate is found by determining the slope of the creep curve in the secondary creep stage; Creep rate = Δε / Δ t (7)

Tensile test:

After longitudinal fixing of the specimen by the upper and lower jaws of the equipment, a tensile load was applied, at rate of (5KN) with velocity of (2mm/min). By utilization of the connected graphic plotter, Model 1195 (INSTRON), the relationship of (P – Δ L) was

obtained.

This relation was then modified to stress – strain (S – e) relationship, which is used to calculate the ultimate tensile strength (UTS) and Young's modulus for the specimen under test.

$$S_* = p / A \quad \dots (8)$$

$$e_* = \Delta L / L \quad \dots (9)$$

Experimental results&discusson

I-V Characteristic:

As shown in figure (4), the variation of the current is a function of the applied voltage for the EP/glass fiber/PANI composite preparing in our method. It can be noticed the current increases steeply with the applied voltage. Where the high value of current obtained is (1.955 mAmp) at the applied voltage (30 Volt). 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 prepared composite shows a linear relationship indicating that power dissipation was negligible within the composite and the calculated conductivity represents the intrinsic conductivity of the composites [13]. We can obtain the value of the electrical conductivity from the reciprocal slope(R) and applying it in equation (2). The important notices, polyaniline have been reported to be stable under ambient condition yet.

Hall Effect

Hall Effect measurement was carried out for EP/glass fiber/ PANI composite. The results indicate that composite is p-type behavior (sign of VH is positive). Figure (5) shows the variation of the current with the Hall voltage for sample. The carrier mobility is about ($7.9 \text{ m}^2/\text{V}\cdot\text{s}$) and the number of the charge carrier is about ($0.007 \times 10^{19} \text{ m}^{-3}$).

Mechanical characteristics

The reason of using this study(creep behavior, tensile test) is due to the poor tensile strength and poor creep resistance may cause deformations of the composite morphology and destruction of the linkage between PANI moieties and chains which leads to various increases in the composite resistivity (low conductivity)

Creep behavior

Creep is the progressive deformation of a material when exposed to constant load .Creep strength of the material is highest stress that a material can stand for a specified period of time without excessive deformation [12]. The creep mechanism is sufficiently complex so that no direct correlation is

established between the creep behavior of any given material and its other mechanical characteristics, such as tensile and yield strengths, hardness, plasticity...etc. Therefore, creep properties of the composites are necessarily to be determined experimentally, either in actual service or through long time tests under static loads of ambient temperature.

The static load (20 N) was chosen to find out the creep characteristics of the sample under test. The behavior of composites is represented in figure (6). If a focusing is made on this figure which represents the EP/glass fiber composite without any treatment and the composite that prepared in our method. It is observed, that the response of these composite to constant stress, as for other materials, is an instantaneous elastic strain followed by viscous time –dependent strain, after an interval of time, and when the stress removed, the dimensions of the sample belong to original dimension with simple varies in length, this mean the elastic strain recovers immediately, this composite is described by standing up to creep test. This mechanism is attributed to the relocation of molecular chains of a material under stress from the sites with higher strain energy to the sites with lower strain energy [13]. The creep rate for this EP/glass fiber composite without any treatment is ($1.56 \times 10^{-6} \text{ min}^{-1}$) lower than that treatment with PANI.

That has value ($2.02 \times 10^{-6} \text{ min}^{-1}$). This result indicates that the mechanical performance and technological potential of PANI conducting polymer composites can

be significantly increased by the development of composite with high-performance polymers.

Tensile strength and young's modulus

Tensile characteristic is the most widely reported mechanical properties of any material. Tensile strength is the maximum load that the sample will carry before breaking under a slowly applied gradually increase load during a tensile test [13].

An Instron machine was used for this test which was carried out at a crosshead speed of 2(mm.min⁻¹). Figure (7) shows the stress-strain curves for EP/glass fiber composite and PANI composite. In generally, it is known that epoxy is a hard, brittle material, and it fractures in a brittle mode. From the stress-strain curves of the all composites. It is quite clear that this composite display plastic deformation behavior, in spite of containing high percentage of brittle material (EP), and although the curve of composite do not display the yield points. The evidence of these ductile behaviors is the occurrence of necking, followed by homogeneous drawing of the sample.

This would lead to the conclusion that when the EP is mixed with 20% of glass fibers its fracture mode will be changed from brittle to ductile, which means reducing the risks of brittle catastrophic failure during application.

Young's modulus of the composite that calculated from the slope of stress-strain curves, we can notice that young's modulus and the Ultimate tensile (UTS) strength values of the EP/glass fiber composite (7923.3 MPa)(375.032

MPa) higher than the EP/glass fiber composites treatment with PANI (5410.5 MPa)(272.661 MPa) respectively. The greater Young's modulus, the smaller elastic strain resulting from application of a given stress [14].

Conclusions

The applied method of preparing PANI composite is successful to obtain electrical conducting composites.

The conductivity of PANI composites lies in the semiconductors. From studying Hall Effect, it was found the type of the charge carriers of the composite is p-type and from mechanical test, it was found that these composites have creep resistance and have high value of ultimate tensile strength (UTS) and high Young's modulus.

It must be noticed that the conductivity shows good stability with time, the good stability in both electrical and mechanical properties leading to diverse the PANI application not only as antistatic and shielding equipments.

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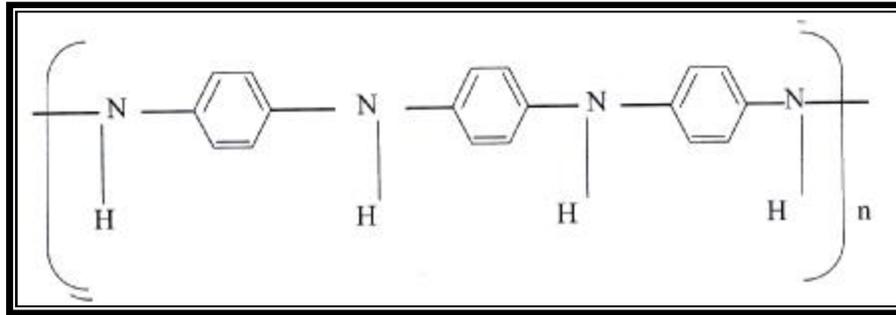


Figure (1) The chemical structure of polyaniline



Figure (2) Image for shape the composite after preparing method



(a)



(b)

Figure (3) (a)Morphology of EP/glass fiber composite without treatment
(b) Morphology of EP/glass fiber composite after treatment with PANI

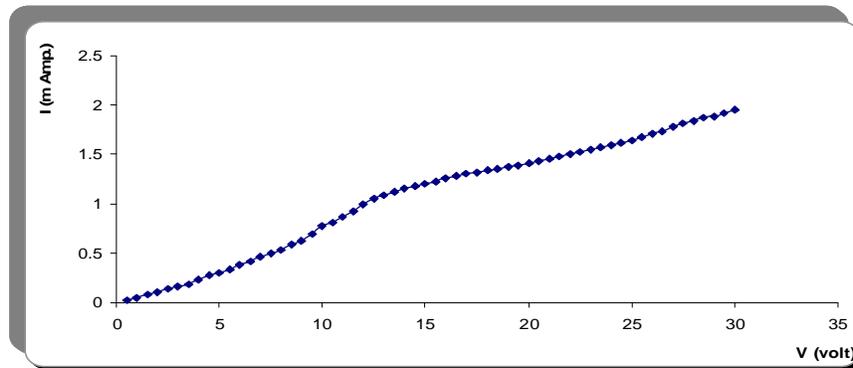


Figure (4) I-V characteristic of EP/glass fiber/PANI composites

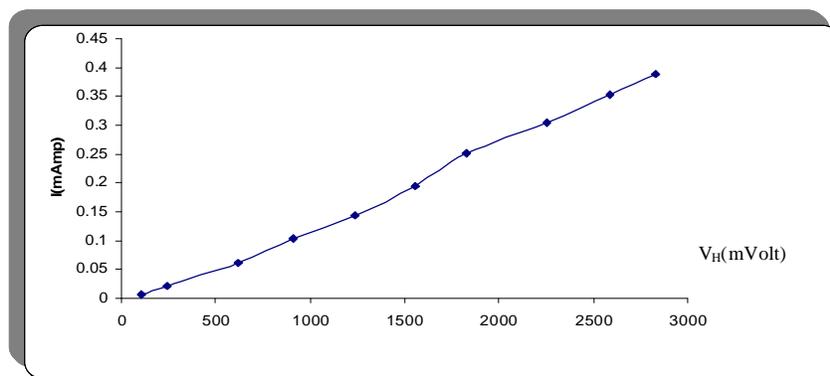


Figure (5) experimental variation of current (I) versus Hall voltage for EP/glass fiber/PANI composite

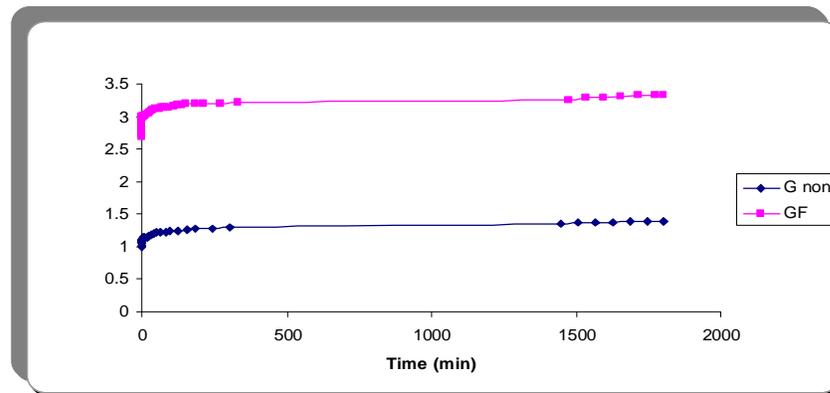


Figure (6) Creep behavior of EP/glass fiber without any treatment composites (GF non) and EP/glass fiber/PANI composites(GF).

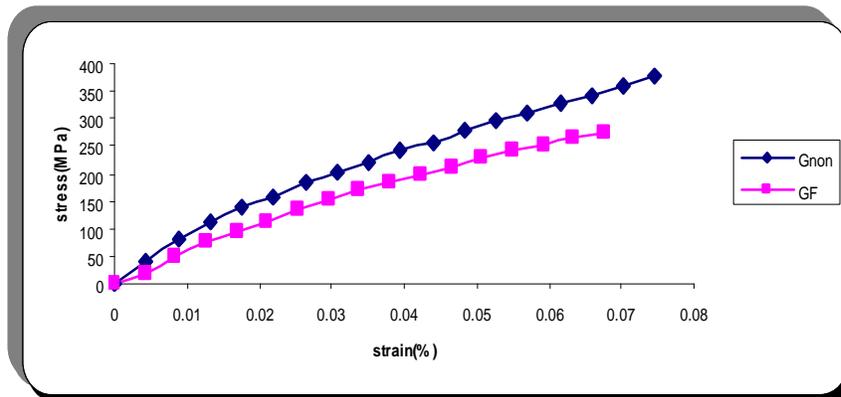


Figure (7) Tensile (stress-strain) curves of EP/glass fiber without any treatment composites (GF non) and EP/glass fiber/PANI composites(GF).