Enhancement of Thermal Stability and Wettability for Epoxy/Cu Coated Carbon Fiber Composites

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Abstract

This research study the effect of surface modification and copper (Cu) coated carbon fiber (CF) surface on thermal stability and wettability of carbon fiber/epoxy (EP) composites. The TGA results indicate that the temperature of 5% weight loss ($T_5$) for Ep/Cu coated CF composite increased to 322 °C when compared with Ep/CF and Ep/chemical treated CF composite. The temperature of 10 wt.% ($T_{10}$) and the degradation temperature ($T_d$) of the Ep/CF composite were 266 and 522°C, respectively, with the chemical treatment and Cu coating. $T_{10}$ and $T_d$ of Ep/CF significantly increased to (310.3, 345 and 543, 565.5) °C. Ep/CF composites showed lower thermal conductivity than that of Ep/Cu coated CF composite. After heat treatment, thermal stability and thermal conductivity of Ep/modified CF composite increased.

The contact angle for CF decreased slightly after chemical treatment to 105°. After Cu electroless coating, the carbon fiber showed a contact angle of 82°. Heat treatment significantly improved the wettability of Cu coating CF showing 32° of contact angle at 250°C.

Keywords

Reducing agent, carbon fiber modification, copper plating, complexing agent.

Articleinfo.

Received: Sep. 2020
Accepted: Nov. 2020
Published: Dec. 2020

Teعزير الاستقرار الحراري وقابلية الترطيب لمتراكبات الإيبوكسي/ألياف الكربون المطلية بالنحاس

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قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

يدرس هذا البحث تأثير تدوير السطح وطلاء سطح ألياف الكربون (CF) بالنحاس (Cu) على الاستقرار الحراري وقابلية الترطيب لمتراكبات ألياف الكربون/الإيبوكسي (Ep). تشير نتيجة التحليل الحراري الوزني (TGA) بزيادة نسبة فقدان الوزن بنسبة 5٪ لتمتراكبات الكربون المطلية بالنحاس ($T_5$) إلى 322 درجة مئوية عند مقارنتها بتمتراكبات الكربون المطلية بالإيبوكسي ($T_5$). ودرجة حرارة التحلل ($T_d$) لتمتراكبات الكربون المطلية 266 درجة مئوية، على التوالي، مع المعالجة الكيميائية والغليف بالنحاس، تزداد و$T_5$ لمتراكبات الكربون المطلية بالإيبوكسي/ألياف الكربون بشكل ملحوظ إلى (310.3، 345 و 543، 565.5) درجة مئوية. أظهرت ألياف الكربون المطلية بالإيبوكسي/ألياف الكربون موروثية حرارية أقل من ألياف الكربون المطلية بالإيبوكسي/ألياف الكربون المطلية بالنحاس. تحسين الاستقرار الحراري، تم تحسين الاستقرار الحراري، تم تحسين الاستقرار الحراري بالعديد من مرات معالجة الجملة إلى مترات الاستقرار الحراري. زاوية التماس لألياف الكربون تختلف بين (0.3) و (1.3) درجة. بعد المعالجة الكيميائية، وظفت ألياف الكربون 82 درجة من زاوية التماس. أدت المعالجة الحرارية إلى تحسين قابلية الترطيب بشكل كبير لألفي الكربون المطلية بالنحاس حيث تظهر 32 درجة من زاوية التماس عند 250 درجة مئوية.
Introduction
Carbon fiber/polymer composite (CFPC) materials are used in many technological industries because of their low density, high strength to weight ratio and high stiffness [1].

Many of the research conducted in the field of improving the properties of composites focused on improving the properties of the base material (matrix) [2]. However recently, research has been directed to improve the properties of the reinforcement phase in order to improve toughness, heat transport and interfacial adhesion between the matrix and fibers [3].

Metal-coated carbon fiber can be used for this purpose to improve wettability, to increase the lifetime of a part by increasing heat transport, to reduce hot spots and to reduce thermal stress by dispersing the heat [4].

Metal coating can be applied in different ways, such as electrodeposition, thermal evaporation, dipping and electroless plating [5, 6]. Electroless plating has been recognized as one of the most attractive and best ways to apply coatings on none or semiconducting surface. It is a process of depositing thin layer of metals, salts, oxides or any other compounds used in various industrial and technological applications. A redox reaction between a metal salt and a formaldehydes reduction in the same solution, a metal coating on surface can be formed in the absence of external current flow [5].

Over recent years, many researchers focused on using copper for coating fiber, glass and polymers due its excellent thermal conductivity and it’s have the functional hydroxyl and carboxyl groups [7].

In many work, catalyst metal seeds such as platinum or palladium, which are relatively of high cost of production, are attached to the surface to cause the activation of the surface [8, 9]. However, the activation in this work was done using silver which is of low cost of production, and an attempt to make of pre-treatment (sensitization and activation) onto the surface of carbon fiber make the activation of the surface be successful.

Experimental work
Distilled water and acetone were used to clean the mat of carbon fiber, which was etched with sulfuric acid (3M H₂SO₄). The carbon fiber was sensitized using tin chloride solution containing (44 g SnCl₂+ 77 ml (3M HCl)), dried at 35 °C for 15 min and activated using silver nitrate solution containing (20gm AgNO₃ + 50ml (3M HCl)).

The copper plating solution was prepared by dissolving (1.3 gm copper sulfate as the main salt in 20 ml of distilled water) and stirred for 20 min to which a complex agent solution (2.6 g of Ethylenediaminetetraacetic acid disodium salt (Na₂EDTA) + 20 ml of distilled water) was then added. This was followed by adding sodium hydroxide solution (1.5gm NaOH+ 30 ml of distilled water) and 15 ml of Hydrazine monohydrate (N₂H₄·H₂O) was added drop wisely. 0.1 ml of Formaldehyde was then added as a reducing agent. Finally, the remaining 40 ml of distilled water was added.

The carbon fibers mat was kept in the prepared solution (of pH approximately equal 12). After chemical plating, the carbon fibers were placed in an oven for drying and heat treating at (150, 200, 250) °C for 1 hour. Table 1 shows the function of used material.
Table 1: List of materials used and its function.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Function</th>
</tr>
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<tbody>
<tr>
<td>Composites</td>
<td></td>
</tr>
<tr>
<td>Carbon Fiber</td>
<td>Reinforced material</td>
</tr>
<tr>
<td>Epoxy matrix</td>
<td></td>
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<tr>
<td>Carbon fiber chemical treating solution</td>
<td>etching</td>
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<tr>
<td>sulfuric acid (H₂SO₄)</td>
<td></td>
</tr>
<tr>
<td>tin chloride (SnCl₂)</td>
<td>sensitization</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>silver nitrate (AgNO₃)</td>
<td>activation</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>Copper chemical plating path</td>
<td></td>
</tr>
<tr>
<td>(copper sulfate CuSO₄)</td>
<td>Cu metal source for plating</td>
</tr>
<tr>
<td>disodium ethylenediamine</td>
<td>complexing agent</td>
</tr>
<tr>
<td>tetra acetate (EDTA-2Na)</td>
<td></td>
</tr>
<tr>
<td>sodium hydroxide (NaOH)</td>
<td>PH adjuster</td>
</tr>
<tr>
<td>Hydrazine monohydrate</td>
<td>Stabilizer</td>
</tr>
<tr>
<td>(N₂H₄·H₂O)</td>
<td></td>
</tr>
<tr>
<td>(Formaldehyde HCHO)</td>
<td>Reducing agent</td>
</tr>
</tbody>
</table>

The composite was prepared by Hand layup process. Initially, one layer of carbon fiber mat was placed in a mold where a thin layer of anti-adhesive coat is applied for easy extraction. The Epoxy resin material is applied using a brush on a reinforcement material. The composite’s specimens were cured at room temperature for 24 hr to reach complete hardening. After that the composites were kept in the oven to complete curing at 70 °C.

Thermal stability of the composites was evaluated with a thermogravimetric analyzer (TGA) (STA PT1000). The samples were heated from 0 °C to 700 °C with a heating rate of 10 °C/min.

Thermal conductivity coefficient was measured using a Lee’s disk. The samples used for thermal tests were cut to the same diameter as the copper plates of 40 mm and to a thickness of approximately 30mm.

Contact angle measurements were performed with a Rame-Hart instrument. An epoxy droplet is injected on the CF surface, and high resolution (60 fps) video camera captures the image of the epoxy droplet, and then analyzes the images.

**Results and discussion**

The elemental composition of the deposit was verified by energy dispersive X-ray (EDX) spectroscopy Fig.1. In addition to the carbon peak originating from the carbon substrate only copper features were noticed, presumably formed as an artifact due to manipulating with the copper-coated CF [10].
Fig. 1: EDX spectroscopy of Cu coated CF.

Fig. 2 and Table 2 show the TGA results for Ep/CF, Ep/chemical treated CF and Ep/Cu coated CF composites at different treatment temperatures have a 5% weight loss ($T_d$) below 450°C, due to the physically decomposition and adsorption of water [11, 12]. It can be noted that, for Ep/Cu coated CF, the temperature for the 5% weight loss increased to 322°C when compared with that of the Ep/CF and Ep/chemical treated CF. This is due to the enhancement of interfacial adhesion after chemical treatment and Cu coating [12].

Fig. 2: Thermal analysis data of Ep/CF, Ep/chemical treated CF and Ep/Cu coated CF composites at different treatment temperatures (150, 200, 250)°C.

Table 2: Thermal analysis data of Ep/CF, Ep/chemical treated CF and Ep/Cu coated CF composites at different treatment temperatures (150, 200, 250)°C.

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ [°C]</th>
<th>$T_5$ [°C]</th>
<th>$T_{10}$ [°C]</th>
<th>$T_d$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ep/CF</td>
<td>76</td>
<td>246</td>
<td>266</td>
<td>522</td>
</tr>
<tr>
<td>Ep/chemical treated CF</td>
<td>83</td>
<td>298</td>
<td>310.3</td>
<td>543</td>
</tr>
<tr>
<td>Ep/Cu coated CF</td>
<td>88.5</td>
<td>322</td>
<td>345</td>
<td>565.5</td>
</tr>
<tr>
<td>Ep/Cu coated CF at 150°C</td>
<td>92</td>
<td>365.3</td>
<td>382</td>
<td>578</td>
</tr>
<tr>
<td>Ep/Cu coated CF at 200°C</td>
<td>96.2</td>
<td>392</td>
<td>409</td>
<td>591</td>
</tr>
<tr>
<td>Ep/Cu coated CF at 250°C</td>
<td>102.3</td>
<td>432</td>
<td>465</td>
<td>602</td>
</tr>
</tbody>
</table>
The temperature for 10 wt.% (T_{10}) and the degradation temperature (T_d) are obtained from Fig. 2. As it can be seen, T_{10} and T_d of the Ep/CF are 266 and 522 °C, respectively. With the chemical treatment and Cu coating, T_{10} and T_d of Ep/CF significantly increased to (310.3, 345 and 543, 565.5) °C, respectively. Thermal stability of Cu coating CF was enhanced because of the thermal stability of Cu and the strong interaction bonds after chemical treatment. This agrees with the results of Bard et al. [11] and Mohd et al. [13].

TGA curves showed that the treatment temperature enhanced thermal stability of Ep/CF, this is due to the oxidation during heating [12].

Fig. 3 shows that Cu plating increased the composites conductivity which may be due to changes in contact resistance at the interface due to chemical modification and copper plating and tunneling resistance [12, 14]. The tunneling resistance between the Cu layer and CF is much smaller than that between copper and epoxy matrix. This effect, then leads to enhancing the thermal conductivities of the coated CF/Ep composites [14].

Fig. 3: Thermal conductivity of different type of Ep/CF composites.

Fig. 4 shows that the thermal conductivity increases as the treatment temperature increase. This behavior is due to the increase of the deposition rate of copper as the temperature increases, which is due to a uniform and continuous dispersion with higher mechanical and chemical bonds [14, 11].

Fig. 4: Thermal conductivity of Ep/Cu coated CF composites at different treatment temperatures (150, 200, 250) °C.
Fig. 5 shows the contact angle of an epoxy drop on Ep/CF, Ep/chemical treated CF and Ep/Cu coated CF composites at different treatment temperatures. The contact angle slightly decreased after chemical treatment to $105^\circ$. This is due to the change in the surface morphology and chemistry during the chemical etching which led to a more hydrophilic behavior. It seems likely that the specific contact surface increased due to material removal which had a great effect on the contact angle [15].

Coating the carbon fiber with Cu greatly improved the epoxy affinity and hence the surface energy. After electroless plating, the carbon fiber showed $82^\circ$ contact angle, which indicates the increase of surface polarity caused the remaining wetting capability of the surface [16].

Heat treatment significantly improved wettability to a strong hydrophilic surface showing $32^\circ$ of contact angle at $250^\circ$C. Also it caused the increase of oxidation of a metal causing the rapid contact angle to decrease and this can strongly enhance wettability [16, 17].

Conclusions
The most critical problem of using fiber in the polymeric systems for electronic applications is compatibility, the interface control between them and the problems of thermal dissipation.

In this work, carbon fiber was modified with metal (Copper), since copper has high surface energy which allows extensive wetting with fiber and matrix. On the other hand, the high thermal conductivity of copper may increase the heat dissipation of composites.

The carbon fiber was etched by using $\text{H}_2\text{SO}_4$. Tin chloride and silver nitrite solution were used to pre-treat (sensitized and activated) the carbon fiber surface, respectively, then an electroless plating method was used to apply copper (Cu) on the surface of carbon fiber.
The thermal conductivity, thermal stability and wettability of prepared Cu modified CF/epoxy composites were notice to improve at different treatment temperatures (150, 200 and 250) °C.

Acknowledgement
The author’s would like to express my special thanks to the material science lap staff in department of physics, college of science, university of Baghdad.

References