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Metallizing Polyetherimide Resin Reinforced with Glass Fibers

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Abstract. The process of surface modification and metallizing polyetherimide resin reinforced with 20% glass fibers was studied and characterized. The objective of the metallization was to eliminate the electromagnetic interference (EMI). The surface of the plastic was modified by etching the resin matrix and then the glass fibers using two different solutions. During the resin etching step, glass fibers were exposed at the surface and then removed by glass etching step. Glass fibers etching was found to be essential to promote adhesion between the metallic film and the resin surface. Also, the heat treatment to remove excess moisture and to relieve stresses was found to be an essential step immediately after the electroless deposition step. After electroplating, the adhesion force between the metal and the substrate was 230 kg/cm^2 (3000 psi).

Keywords: Plastic metallization, Metal adhesion, Polyetherimide, EMI.

Introduction

Metallizing of plastics is a growing technology to fulfill different applications and requirements. One of the main applications for metallizing plastics is to shield the plastic parts and its contents against electromagnetic interference (EMI), especially in electronics industry and electric circuits that are sensitive to EMI. Usually, 1 to 2 micrometers of copper or nickel deposited on the plastic surface are sufficient to provide an EMI shield [1, 2]. Nickel is deposited on top of copper for corrosion protection.

The process of plastic plating involves several standard steps and each step provides certain function or add certain property to the plastic surface [3]. Etching in chromic-sulfuric acid mixture is an essential step for metal adhesion. During the etching step the surface is etched to provide a micro-rough surface to anchor the metal layer to the plastic surface. Other adhesion mechanisms between the plastic surface and the subsequent metal layer have been discussed and studied in the literature [4-6]. Sensitizing and catalyzing the surface with tin and palladium solutions is the second main step. This involves deposition of Pd nuclei to act as centers for further deposition during the electroless process. Finally, the catalyzed plastic surface is ready to be metallized using the electroless solution (either nickel or copper). Acrylonitrile-butadiene-styrene (ABS) plastic is the most common plastic type used for plating. ABS is commonly used for plastic plating due to the large adhesion force obtained between the plastic surface and the metallic film. Such adhesion force rises due to the uneven etching of the styrene and butadiene phases resulting in a micro-roughness that provides a key to promote adhesion [1-3].

However, the process of metallizing other types of plastics involves more steps to pre-treat the plastic surface prior to the final electroless plating step. In the case of single phase amorphous plastics, generally poor adhesion is found to result between the metal films and the plastic substrate which limits the application of such materials in plastic plating [7-10]. However, certain families of plastic materials can be fiber reinforced, e.g. using glass, to improve strength and are also found to improve the adhesion of the metal film after plating. Polyetherimide (PEI) reinforced with glass fibers is an important material that has undergone further investigation to optimize the plating process. PEI is used in several applications, such as in printed circuit boards and electrical circuit components housings, intended for use in long life-time applications, and having high quality standards. Nevertheless, in certain cases it is essential to metallize the surfaces of these composites for EMI shielding, so as to work effectively in the proper frequency range [1, 8, 11].

In this paper, a process for metallizing polyetherimide reinforced with 20% glass fibers is presented and discussed. The effect of the different processing steps on the microstructure of the composite's surface is discussed, along with the effect on the resulting adhesion properties between composite and metal plating.

Experiments

Injection molded samples of PEI reinforced with 20% glass fibers were used in this study to investigate the effect of each treatment step on the surface microstructure. The size of each sample was 10 cm long by 5 cm wide and 3 mm thick. Molding conditions of polyetherimides are important and greatly affect subsequent metallizing process. Molding temperature (between 350 and 400ºC) is the most important parameter during molding to achieve desired adhesion values [1]. Other conditions of molding operation should be exactly followed and recorded to obtain reproducible results.

The main optimized steps to metallize polyetherimide reinforced with glass fibers are; the initial heat treatment process, preconditioning for swelling, etching of the resin, glass etching, then activation and catalyzing. Finally, electroless copper and nickel were applied on the surface. After each step sufficient rinsing must be applied to ensure limited subsequent solution carry over.

The main steps employed in metallizing process are shown in Table 1. The most important steps are etching step to promote metal layer adhesion and surface catalyzing with palladium to initiate deposition. The details of these processes are given in the next section.

Table 1. Main steps involved in metallizing polyetherimide reinforced with 20% glass fibers

Process	Time (min)	Temperature (^oC)
Heat treatment	90	160
Preconditioning 700 ml maculidiser* + 300 ml ethylene glycol	12	25
Etching 400 g/l Cr_2O_3, 200 mL/L conc. H_2SO_4	12	75
Neutralizer 23 g/L $NaHSO_3$ 35 mL/L conc. HCl	4	25
Glass etch 10 g/L NaF 70 mL/L conc. H_2SO_4	8	30
Activator*	3	30
Accelerator*	2	50
Electroless copper*	30	45
Electroless nickel*	10	25
Final heat treatment	60	160

* Chemicals are proprietary from MacDermid-Canning, which are commonly used to metallize ABS plastics.

Electroless plating is the final step to metallize the surface and it is largely affected by pretreatment of the surface. Some of the used chemicals, copper and nickel electroless solutions, were proprietary chemicals form McDermid-Canning. Nevertheless, these chemicals are based on copper formaldehyde systems and nickel hypophosphate.

After each metallizing step, the sample surface was imaged by scanning electron microscope from Joel model 845 and by an optical microscope from Olympus. Also, the quartz crystal microbalance (QCM) was used to determine the deposition rate of both the copper and nickel electroless solutions to ensure sufficient coverage over the substrate. QCM has been used in the past successfully to simultaneously measure the deposition rate at the surface [13]. The adhesion force between the metal layer and the substrate was measured by the pull method. In this method, a wire is soldered to the metallic surface then a pull force is applied until the wire is detached from the surface leaving the PEI substrate exposed. The pulling force is defined as the force necessary to detach a welded wire from the metal plated surface. The exposed area and the maximum force are measured then the ratio between the maximum pull force and detached area is the adhesion force.

Results and Discussion

The surface of the molded, untreated PEI is shown in the SEM photomicrograph (Fig. 1). Its surface was rough and contained many protrusions due glass fibers; however, most of the glass fibers were covered by the resin. In the following section, each main process step will be discussed in relation to resulting surface microstructure.

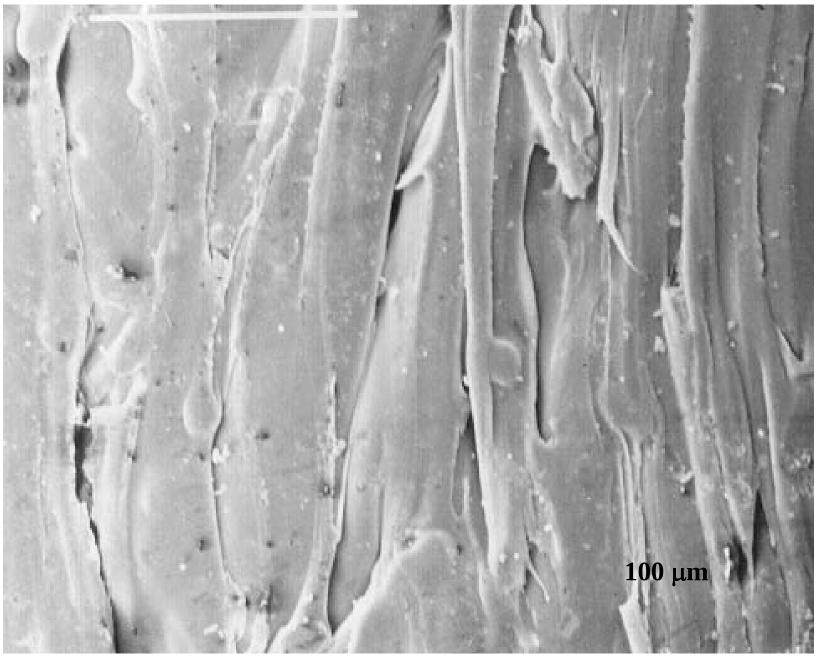

Fig. 1. Scanning electron micrograph of the initial PEI surface.

1. Initial heat treatment

It was found that the initial heat treatment at 160 ^{o}C for 1.5 hour was an important step to promote adhesion and to prevent subsequent delaminating of the metal layer. It is suggested that such heat treatment removes excess moisture in the bulk of the resin and probably relieved the substrate from any stresses. The surface microstructure did not appear to be altered after heat treatment, as indicated by the SEM photomicrograph (Fig. 2).

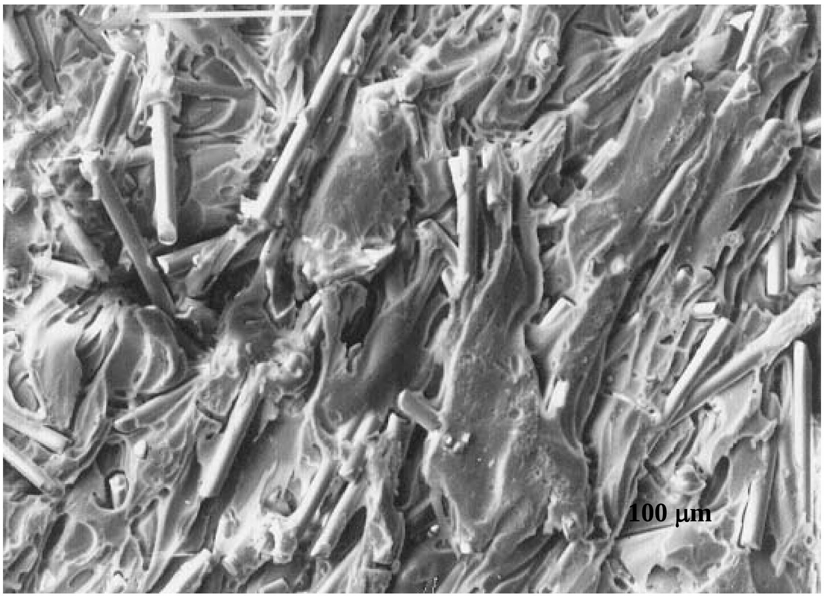

Fig. 2. Scanning electron micrograph of the PEI surface after chromic acid solution treatment.

2. Swelling process

During this step the matrix of the polyetherimide-glass fibers was opened to allow effective etching process and to improve the wetting ability of the polyetherimide resin. The surface microstructure was not altered after this step. However, subsequent etching was improved by this step.

3. Etching process

The resin surface was etched by chromic oxide and sulfuric acid solution and the resulting surface microstructure is shown in Fig. 2. The glass fibers on the surface were completely exposed as shown in Fig. 2. Also, Fig. 3, an optical image of the surface, confirms the exposure of the glass fibers Fig. 3 indicates clearly the glass fibers location where the clear glass reflection in the image is indicated. This resulted because the chromic acid solution did not react with glass while it etched the PEI surface leaving the glass fibers exposed on the surface. The typical diameter of the glass fibers as indicated in Figs. 2 and 3, was 10 μm which is the same as the supplied glass fibers diameter. Also, the length of the glass fibers was found to vary between 50 μm to 500 μm. The effect of etching of PEI on the adhesion mechanism is not very well understood**.** However, previous investigations on the effect of etching of the resin contact angle suggest the presence of an increased number of functional groups with polar characteristics at the surface [12]. However, with the added presence of glass fibers, the adhesion mechanism was due to the combined action of the chemical and mechanical anchoring.

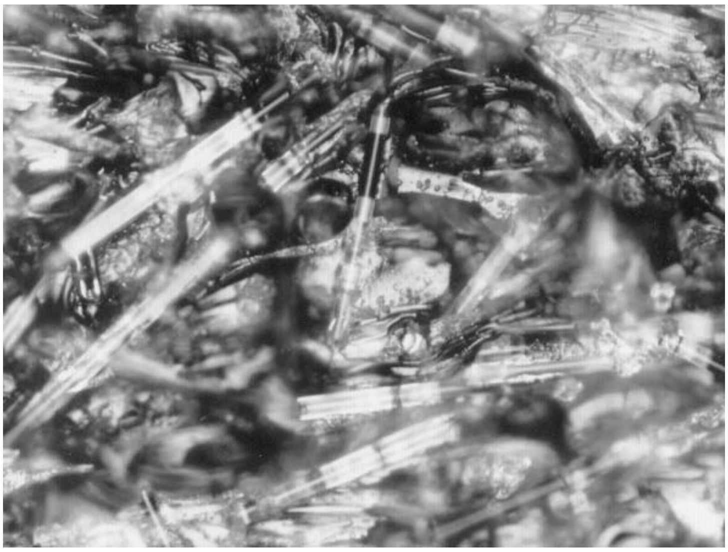

Fig. 3. Optical image of the PEI's surface after chromic acid solution treatment. Glass fibers are clearly indicated in the image. At 200x magnification.

4. Neutralizing step

This is a process which did not affect the surface microstructure. However, this step was to remove excess chromate from the surface and to neutralize the plastic surface.

5. Glass etching

The glass etching process is an essential process for glass reinforced resins. In this process the exposed segments of glass fibers were etched and removed from the surface**.** Fig. 4 shows the effect of etching and removal of excess glass fibers from the surface to improve adhesion to the surface. The presence of loosely attached glass fibers lead to weak adhesion sites once covered in metal plate and so the metal film maybe easily removed from such locations.

Subsequent operations to metallize the PEI matrix were similar to the ABS metallizing steps, i.e. the activation and acceleration steps. Electroless copper was deposited at an average rate of 0.9 um/hr, as obtained from the QCM results shown in Fig. 5. For corrosion protection, electroless nickel was deposited on top of the electroless copper film. An electron photomicrograph of the copper film after electroless deposition is shown in Fig. 6. Small micro-cracks can be seen in the image. These were observed also at early stages of deposition. This indicated that the copper film was not total conformal and led to cracking due to the rough topography of the surface and entrapment of the electrolyte in the micro-cracks of the surface. Finally, the last heat treatment

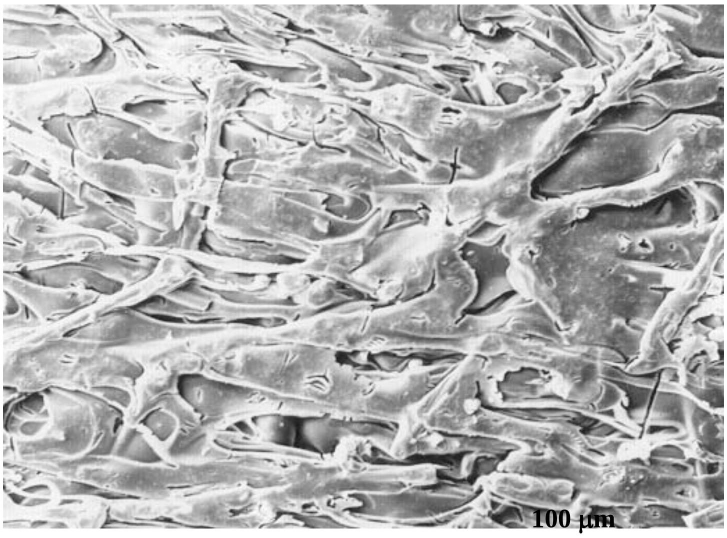

Fig. 4. Scanning electron photomicrograph of the PEI surface after glass etching treatment.

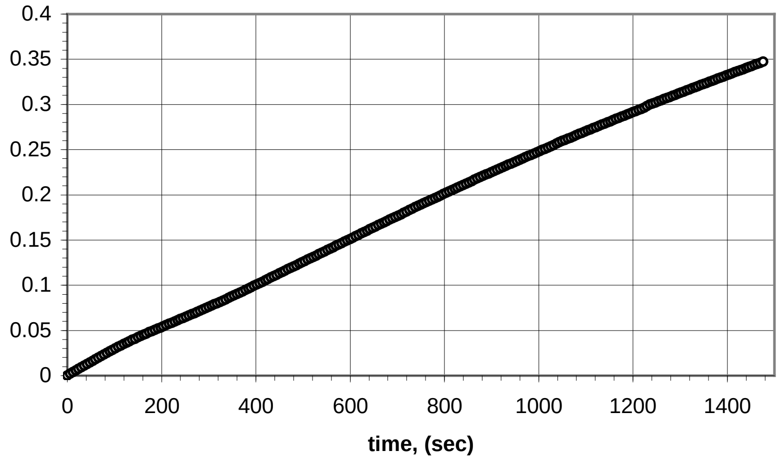

Fig. 5. Quartz crystal microbalance result for copper electroless solution.

process was found to be an essential step to maximize the adhesion of the metal layer. It was believed that such process removes excess moisture in the micro-cracks leading to better adhesion. The surface microstructure remains the same after heat treatment and no variations was observed.

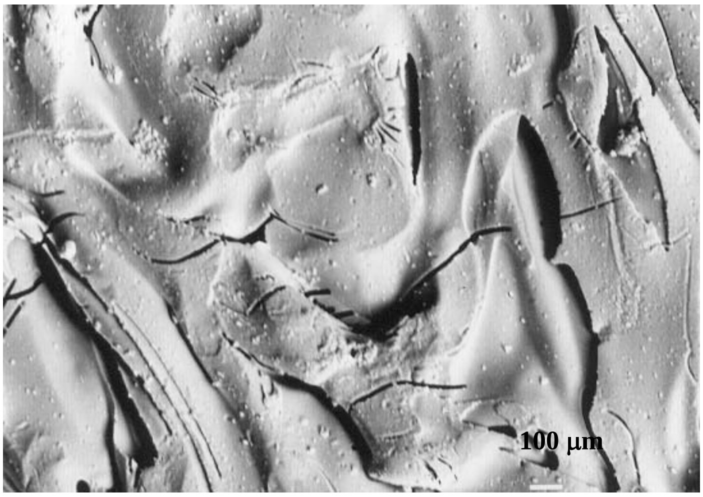

Fig. 6. Scanning electron photomicrograph of electroless copper deposited on treated PEI surface.

In general, the obtained metallic film was adherent to the surface and the adhesion force was about 230 kg/cm^2 (3000 psi). The surface was relatively dull and had limited brightness due to the roughness of the underlaying treated PEI. The heat treatment process, especially the final heat treatment step, was found to be an essential step to promote and increase the adhesion force. The adhesion force was increased from values between 190 to 230 kg/cm^2 (2500 to 3000 psi) due to the final heat treatment step.

Conclusion

Glass reinforced polyetherimide resin has been subjected to a series of novel surface pretreatments, prior to electroless plating with copper and then nickel. The resulting modified surface microstructure indicated that glass fiber etching is an essential step to improve adhesion between the PEI and the metal plate . Also, it was found that heat treatment before and after the metallizing step are important steps to promote adhesion.

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ترسيب المعادن على سطح بوليمر الايثرايميد المقوى بألياف الزجاج

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ملخص البحث. تمت دراسة تحسين و ترسيب النحاس و النيكل على سطح بوليمر الايثر ايميد المقوى بالألياف الزجاجية و ذلك بطريقة الترسيب اللاكهربائي. من أهداف الترسيب المعدني يكون عادة لمنع التداخل الكهرومغناطيسي من العبور خلال البوليمر. في هذه الدراسة تم معالجة سطح البوليمر كيميائيا بواسطة حمض الكروم بالإضافة إلى مواد أخرى لمعالجة الألياف الزجاجية و ذلك في خطوات منفصلة. من أبرز الخطوات التي ساعدت على ثبات المعدن على السطح كانت معالجة السطح حراريا قبل و بعد الترسيب حيث أصبحت قوة التصاق المعدن إلى سطح البوليمر ما يعادل ٢٣٠ كجم/سم^{٢} .