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Comparison between microwave and thermal curing of a polyimide adhesive end-caped with phenylethynyl groups

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ABSTRACT

Microwave energy was investigated to cure phenylethynyl-end-capped polyimide adhesive using an industrial microwave oven at a frequency of 2.45 GHz and the adhesive properties, thermal performance and curing mechanism for bonding stainless steel were evaluated. The results are compared with those of thermal cured samples. It was demonstrated that while the lap shear strength properties and thermal performance of microwave cured samples were almost as good as those cured via a thermal process, the microwave curing process resulted in a significant reduction in the process cycle time and power consumption. The Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis of the cured resin structures suggested that there was no obvious difference in the chemical reactions taking place during the microwave and the thermal cure processes.

1. Introduction

Aromatic polyimides (PI) have been used in a variety of applications due to their excellent thermal stability, chemical and radiation resistance [1] and have been shown to be promising as high-temperature structural adhesives to meet the demand of modern aerospace, aviation and electronic industries [2–4]. Thermoset PI resins terminated with phenylethynyl groups have recently received considerable attention due to their excellent mechanical and chemical properties as well as the volatile-free nature of the curing process which is pivotal to large area bonding applications. [5–7] Numerous research programs have indicated the potential of these resins as high temperature structural adhesives for metallic adherends such as aluminum [8], titanium alloy [2,3,9] and steel [10,11]. However, the high cure temperature (over 350 °C) and long curing cycle (hours) have been considered a major deficiency for adhesives of this type.

Microwave radiation provides rapid, localized and energy-efficient heating of materials. However, the heating mechanisms associated with microwave are based on the dielectric properties of the materials to be heated. Some microwave energy absorbing agents such as magnetic particles, carbon black, carbon nanotubes, metal particles, or carbon fibers could effectively facilitate heating of epoxy resin and composites through microwave radiation. [12–15] Research has indicated that microwave heating, as compared with conventional heating methods, can be highly productive, where the selective heating of epoxy adhesives and improvement of properties of the cured epoxy adhesive joint can be achieved. [16–18].

In the case of polyimides cured with microwave, only a limited amount of work has been published. Liu et al. [19] investigated the cure of nadic-end-capped polyimide precursors (RP-46 resin) and glass and its graphite composites using microwave energy. The results indicated that microwave energy absorbing agents such as 0.057 wt % chopped graphite fibers, were essential to achieve complete cure. In addition the flexural strengths and moduli of composites cured by microwave irradiation achieved 50 to 80% of the properties of composites fabricated by conventional thermal processes. Fang et al. [20] compared the thermal and microwave processes used to prepare carbon fiber reinforced phenylethynyl-terminated polyimide composites in order to evaluate the advantage of the microwave process. They found that, compared with standard thermally cured composites, microwave-cured composites exhibited higher *Tg*s, flexural strengths and moduli and shear strengths at 177 °C They [21] also reported on the kinetics of the microwave cure of a simple phenylethynyl terminated imide model compound and a phenylethynyl-terminated imide oligomer using a variable frequency microwave furnace. The results indicated that the activation energy of the microwave cure was much lower than that of the thermal cure and a faster cure can be provided by microwave cure. All this research indicated that the microwave cure process should be an effective method to achieve rapid cure of polyimide adhesives.

In this paper, a typical imide oligomer derived from 1,3-bis(4-

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aminophenoxy)benzene (1,3,4-APB), 3,4′-oxydianiline (3,4′-ODA) and 2,3,3′,4′ biphenyltetracarboxylic dianhydride (α-BPDA) and end-caped with phenylethynyl was synthesized as a polyimide adhesive. Microwave- and thermally cured steel-steel lap shear joint coupons were fabricated and the adhesive properties, thermal performance and curing mechanism of this adhesive were evaluated.

2. Experimental

2.1. Materials

Starting monomers 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB), 3,4′-oxydianiline (3′,-ODA) and 2,3,3′,4′-biphenyltetracarboxylic dianhydride (α-BPDA) were supplied by Changzhou Sunlight Pharmaceutical Co., Ltd (China). 4-Phenylethynyl phthalic anhydride(4-PEPA) was supplied by Wuxi Bohai Chemical Co., Ltd (China). 1-Methyl-2-pyrrolidinone (NMP) was supplied by Xilong Chemical Reagent Co., Ltd (China). Toluene, ethanol and acetone were supplied by Beijing Chemical Reagent Factory (China). All materials were used as received, except for α-BPDA, which was dried in a vacuum oven at 170 °C for 8–10 h prior to use. The adherend material used in this study was stainless steel S304 (0Cr18Ni9).

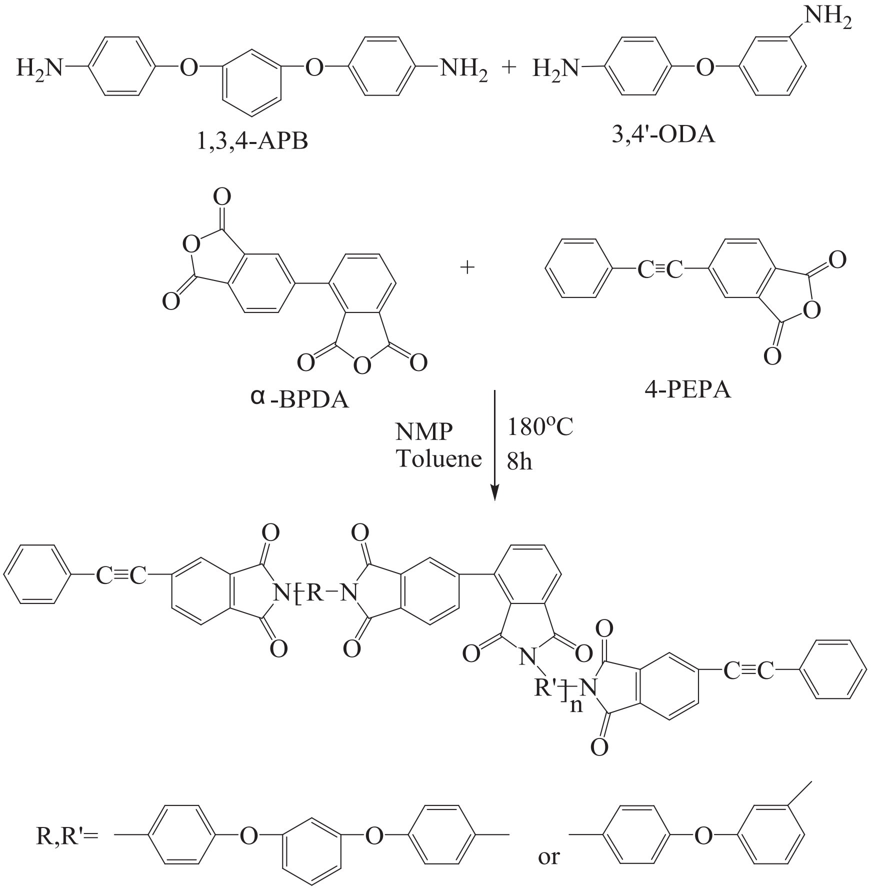
2.2. Synthesis of polyimide adhesive

The PEPA end-capped oligomers from α-BPDA were synthesized according to a published method [5,22] as illustrated by Scheme 1. Diamine monomers 1,3,4-APB (4.38 g, 0.015 mol) and 3,4'-ODA (1.00 g, 0.005 mol) were placed in a dried 250 ml three necked round-bottom flask with 30 ml NMP which was equipped with a nitrogen inlet, mechanical stirrer, and a Dean–Stark trap topped by a condenser. After the diamines were dissolved completely, α-BPDA (3.49 g, 0.0119 mol) was added and the reaction mixture was stirred at room temperature for 1 h under a nitrogen atmosphere. Then PEPA (2.02 g, 0.0162 mol) was added with additional NMP to adjust the solids' concentration to 20% (w/w). The mixture was stirred at room temperature for another 1 h. Then, toluene (15 mL) was added as water-carrying agent. The reaction was processed at 180 °C with stirring in nitrogen for 8 h. Then, the reaction solution was allowed to cool and was poured slowly into an excess of ethanol with vigorous mechanical stirring. The light yellow precipitate was collected by filtration, washed thoroughly with ethanol and water, and dried at 100 °C for 2 h. The collected precipitate was then pulverized to a powder with a pulverizer and dried in a vacuum oven at 150 °C for 2 h, 180 °C for 2 h, and 200 °C for 1 h successively to give a PI oligomer powder with a theoretical molecular weight of 1500. The yield was 8.67 g (85%).

2.3. Preparation of lap shear joint coupons

Lap shear joint coupons were prepared according to our previous study. [23] The steel coupons used in this study were polished with a 1000 grade emery paper to expose a new chemically active surface. The coupons were finally cleaned with acetone and dried with hot air prior to bonding. Lap shear joints were prepared in accordance with ISO standard 4587. The size of the coupon used was 100×25×1.6 mm. The bonded area of the joint was 25×12.7 mm (317.5 mm^2).

The PI/NMP solution prepared with a 25 wt% solid concentration was directly applied on the adherend surface with the help of a dropper. The adhesive coated adherend was then placed in an oven and heated at 50, 100, 150 and 200 °C for 0.5 h at each temperature to remove solvent from the adhesive layer. Subsequent deposited layers were cut to 25×12.7 mm with a similar weight of 0.020–0.022 g in order to control the bondline thickness. And coated substrates outside



Scheme 1. Polymerization of the PI oligomer.