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Effect of superheated steam treatment of carbon fiber on interfacial adhesion to epoxy resin

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ABSTRACT

To elucidate the effect of superheated steam (SHS) treatment of carbon fiber on the adhesion to epoxy resin and surface states, virgin unsized carbon fiber was exposed to SHS with or without N_2 in the temperature range of 500–800 °C. The interfacial shear strength (IFSS) between the carbon fiber and epoxy resin was successfully improved by SHS treatment with N_2, and the IFSS of fiber treated above 700 °C was the same as or higher than that of a commercial sized fiber. SHS treatment without N_2 resulted in an increase of total acidic groups on the fiber surface accompanied with the increase of phenolic hydroxyl groups, whereas that with N_2 resulted in a simultaneous increase of total acidic and basic functional groups. The significant improvement in the IFSS after SHS treatment with N_2 is considered to be due to the increase of basicity on the fiber surface.

1. Introduction

Carbon fiber is widely used for the reinforcement of advanced composite materials due to its high specific tensile strength and modulus. In particular, carbon fiber reinforced plastics (CFRPs) have received much attention for application in the transportation industry to achieve increased fuel efficiency by weight reduction. For example, the structural weight of the latest airliner is composed of over 50% CFRPs [1]. In addition, CFRPs are being applied to the structural components of automobiles [2]. However, there is concern regarding the high production cost of carbon fiber and the increasing quantity of CFRP waste produced in the manufacturing processes and after use. The most effective way to address these issues is to develop a high-efficiency and low-cost CFRP recycling process for the reproduction of CFRPs using recovered fibers.

There have been several approaches to the recovery of carbon fiber from CFRPs. Pyrolysis [3,4], where the matrix resin is decomposed in an inert gas (e.g. N_2), is the most common fiber recovery process. This is a cost-effective process and is capable of treating a large amount of CFRP waste; however, there is a possibility of char deposition onto the fiber surface. Solvolysis with alcohol under ambient pressure [5] has the potential for recovery of the polymer components in addition to the fibers; however, the number of depolymerizing resins is limited. Super-/sub-critical fluid methods [6–8] also enable the recovery of both fiber and polymer components, although there is difficulty in scaling-up the procedure due to pressure vessel requirements.

Superheated steam (SHS) is dry steam at a temperature above the boiling point of water. SHS treatment has received much attention for various industrial applications because of its attractive features. For example, it has a high heat transfer coefficient, which enables rapid and uniform heating of thick and complex shaped specimens. Furthermore, SHS provides a low oxygen partial pressure (Po_2) environment, and therefore the SHS treatment of CFRP waste has the potential to effectively decompose the matrix resin and enable the recovery of carbon fiber without degradation by oxidation. In addition, SHS treatment can be scaled up because it is a process that uses water vapor at ambient pressure. Thus, investigations showing high potential for the recycling of CFRPs using SHS have been reported recently [9–12].

Commercial carbon fibers are typically subjected to surface treatment and then coated with a sizing agent to improve adhesion between the carbon fiber and resin. However, the sizing agent on a fiber surface is generally removed with the CFRP matrix resin during such fiber recovery processes. Therefore, an additional surface modification process after the fiber recovery process is necessary for re-use of the recovered fibers. Although the SHS treatment will

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also remove the sizing agent on fibers; it is also expected to introduce active sites for resin adhesion. Furthermore, the addition of process gas, such as N_2 gas, to SHS should be effective for improvement of the adhesion between fiber and resin. If SHS treatment could enable the simultaneous recovery of carbon fiber from CFRPs without degradation and improvement in adhesion between fiber and resin, then further lowering of CFRP production costs could be expected by the use of recycled carbon fibers without the need for additional surface modification processes. However, it is not sufficient to understand the adhesion properties of fibers after SHS treatment to resin.

In this paper, we have focused on understanding the influence of SHS treatment on carbon fiber as a fundamental study toward the development of CFRP recycling processes using SHS. The objective of the present investigation is to clarify the effect of SHS treatment on the adhesion of virgin fiber to epoxy resin and the resultant surface chemical states. In addition, the influence of N_2 gas addition during SHS treatment is evaluated.

2. Experimental

2.1. Materials

Virgin carbon fiber (TORAYCA®T700, Toray Industries Inc., Tokyo, Japan) without surface treatment and sizing agent (unsized fiber) was used as the test specimen. Ultrasonic cleaning of the unsized fibers was performed sequentially using acetone, ethanol and pure water. Carbon fiber coated with a sizing agent (sized fiber) was also evaluated as a reference specimen.

2.2. Estimation of SHS environment

The stability of carbon materials in the SHS environment was firstly estimated using FactSage thermodynamic equilibrium calculation software (GTT Technologies, Aachen, Germany) [13]. Fig. 1 shows estimations of the equilibrium oxygen partial pressures (Po_2) for SHS generated using H_2O with different dissolved oxygen (DO) and the thermodynamic phase equilibrium boundary for the C—CO, CO_2 system. The DO concentration of the water, which was not controlled by any treatment, was measured to be 7350 µg/L. The estimated Po_2 of SHS generated using H_2O with 7350 µg/L of DO below 900 °C (Fig. 1(c)) is constant, depending on the DO and its equivalence to the measured Po_2 of high purity Ar gas (99.9999%). Carbon is stable in the region below the equilibrium boundary of the C—CO, CO_2 system, so that carbon materials are considered to oxidize in SHS with any concentration of DO. Therefore, if CFRP waste is treated with SHS, it is necessary to kinetically suppress oxidation of the carbon fiber. However, a slight oxidation of carbon fiber without fiber strength deterioration is considered to be beneficial, because it is related to the addition of oxygen-containing functional groups on fiber surface.

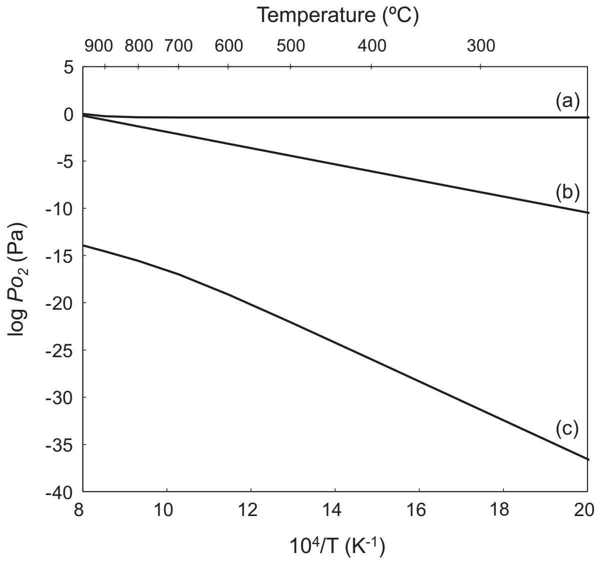

Fig. 1. Equilibrium oxygen partial pressures (Po_2) for (a) SHS generated using H_2O with 7350 µg/L of dissolved oxygen (DO) and (b) that with 0 µg/L of DO, and (c) the phase thermodynamic equilibrium boundary line for the C—CO, CO_2 system.

2.3. SHS treatment procedure

SHS was produced using an induction-heating (IH) system. Saturated vapor is first formed using a steam boiler, and is then heated with pellet-type IH heaters. An IH-type SHS generator has the advantage of precise temperature control and rapid heating, although the constituent materials must have both excellent corrosion resistance to high temperature steam and thermal shock resistance. To generate clean SHS at temperatures above 500 °C using an IH system, electrically conductive $La_{0.8}Sr_{0.2}MnO_{3+\delta}$ [14] was selected as the heater and Al_2TiO_5 ceramic tube was used as the chamber material of the SHS generator. The atmosphere of the SHS can be controlled by the addition of any amount of process gases to the saturated vapor.

Unsized fiber bundles were placed in the upper side of the SHS generator at 400 °C together with the process chamber and then held for 5 min at 500–800 °C. Removal of the specimen with the chamber was conducted at 400 °C. Both the heating and cooling rates were 20 °C/min. The specimen was exposed to SHS at a flow rate of 5 kg/h with and without the addition of 4 vol% N_2 gas.

2.4. Evaluation

Field emission-scanning electron microscopy (FE-SEM; S-4500 and SU-8000, Hitachi High-Technologies Corp., Tokyo, Japan) was used to examine the diameter and surface morphology of the carbon fibers.

The specific surface areas of the carbon fibers were measured by the Brunauer–Emmett–Teller (BET) method using a specific surface area analyzer (AutoSorb-1, Quantachrome Corp., Florida, US). Krypton gas was used as an adsorbate because it has a relatively low vapor pressure, which allows measurement of very small specific surface areas.

Tensile strength testing of single carbon fibers was performed using a universal testing machine (5582, Instron Corp, Norwood, USA) with a 10 N load cell. Tensile strength specimens were prepared by fixing a monofilament onto a paper holder with adhesive. The specimen was set up in the testing machine and the paper holder was then cut into two parts before testing. The gauge length was 20 mm and the crosshead speed was 0.5 mm/min. All tests were conducted at room temperature. Twenty or fifty specimens were tested for the treated fiber or the unsized and sized fibers, respectively.

The interfacial shear strength (IFSS) between the carbon fiber and resin was determined from single fiber fragmentation tests. Flat bone-shaped single fiber composite specimens (50 × 2 mm) were prepared using bisphenol-A type epoxy resin (#828, Mitsubishi Chemical Corp., Tokyo, Japan) and triethylenetetramine (Mitsubishi Chemical Corp., Tokyo, Japan) as the matrix resin and curing agent, respectively. The specimen was strained in steps until no further fragmentation of carbon fiber occurred. The IFSS (τ_i) can be estimated from the Kelly–Tyson model [15]:

$$\tau_i = \frac{\sigma_f(l_c)d_f}{2l_c} \qquad (1)$$