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Preparation and Properties of Oligomeric Siloxane-Grafted Silica Nanoparticles in a Dry Surface Treatment System

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Abstract

For the purpose of the prevention of environmental pollution and the simplification of reaction process, the dry surface treatment system and carefully controlled synthesis of oligomeric siloxane (*oligo*-SiO) was investigated. The grafting of the *oligo*-SiOs onto the silica surface was successfully achieved. The *oligo*-SiOs made by both bifunctional silane and tetrafunctional silane contained many hydroxyl groups that led to the higher chemical grafting efficiency. By grafting of *oligo*-SiO containing moderate number of phenyl groups onto the surface, the silica was easily dispersed in mixed solvent of toluene/ethyl acetate. In addition, the *oligo*-SiO-grafted silica dispersed in a composite polyimide film had excellent adhesion ability to a silicon chip.

Key-words: *Silica nano-particle, Grafting, Dry surface treatment, Oligomeric siloxane, Polyimide*

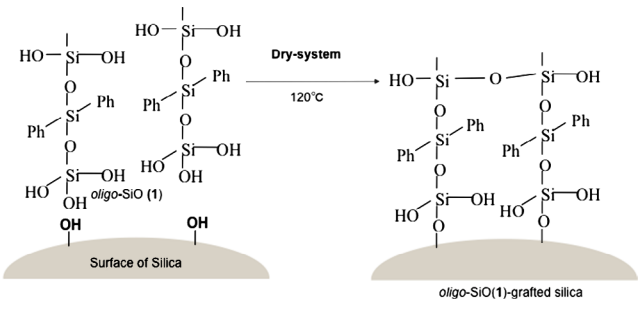
1. Introduction

Accompanying the evolution of the information society, the adhesives for electronic materials are required to achieve high heat resistance and excellent reliability that matches the high density of electronics. The adhesives that have such higher heat resistance and excellent reliability include die bond films, semiconductor sealants and wiring board substrates. The development of adhesives now requires not only the development of new resins, but also the design of surface-modified inorganic particles.

In general, dispersing nanoparticles, such as silica or carbon black, uniformly into a polymer or an organic solvent is very difficult because of aggregation of these particles. We have pointed out that the dispersibility of silica nanoparticles and carbon black is greatly improved by surface grafting, namely, chemical binding of polymers, onto silica nanoparticle and carbon black surfaces[1]. We have also reported the grafting of various polymers such as vinyl polymer, polyester, polyether, poly(organophosphazene), poly(dimethylsiloxane) and poly(oxazoline) onto silica nanoparticle and carbon black surfaces[1]. Takano and his coworkers have reported that heat resistance and reliability of the adhesive were improved by controlled thickness of oligomeric siloxanes on the surface of nanoparticles[2].

However, scale-up production of polymer-grafted nanoparticles was still hardly achieved. The production requires complicated procedures, such as centrifugation, filtration and solvent extraction, which results in the consumption of a lot of waste solvent. We have reported that the scale-up radical graft polymerization of vinyl monomers onto silica nanoparticle surface initiated by azo groups and peroxycarbonate groups previously introduced onto the surface in the solvent-free dry-system was effective to reduce the complicated procedures[3,4]. But there are certain disadvantages to these processes: they still take longer and cost more. It has been reported that several kinds of oligometric siloxanes (*oligo*-SiOs) were effective to improve interfacial properties of inorganic material/polymer composites[5].

One purpose of this study is to make surface grafting of *oligo*-SiO onto silica nanoparticle by only one process. The grafting in a dry-system was successfully achieved by spraying solution of *oligo*-SiO (**Scheme 1**): the *oligo*-



Scheme 1 Preparation of *oligo*-SiO-grafted silica in a dry-system.