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Reaction of 6-(3-Triethoxysilylpropylamino)-1,3,5-Triazine-2,4-Dithiol-Monosodium Salt with Metal Surfaces

Kazuki GYODA*,†, Katsuhito MORI**, Takahiro KUDO**, Kazuhisa TAKAGI*, Shuji OKADA*** and Kunio MORI**

**Asahi FR Laboratories Inc., 2-7-2 Dote, Omiya, Saitama, Saitama 330-0801, Japan*
***Sulfur Chemical Institute Inc., CollaboMIU 306, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan*
****Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan*
†Corresponding Author, E-mail: k-gyoda@asahi-rubber.co.jp

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Abstract

Reactions of the ethoxysilyl and thiol groups of 6-(3-triethoxysilylpropylamino)-1,3,5-triazine-2,4-dithiol-monosodium salt (TES) with Ti, Al, Fe, and Sn metals were investigated. Metals and heating temperatures affect the reaction types of ethoxysilyl and thiol groups, following the ionization tendency series. The ethoxysilyl groups reacted with all three types of metals (series with high, moderate and low ionization tendencies). The thiol groups reacted with the Sn oxide films to produce Sn-S bonds. For Fe and Sn surfaces, SS groups were formed by the oxidation of thiol groups in air. For all metals used here, SO_X groups were observed.

Key-words: *Metals, 6-(3-triethoxysilylpropylamino)-1,3,5-triazine-2,4-dithiol-monosodium salt, XPS surface analysis, Ionization tendency series*

1. Introduction

Connection of various materials via a junction technology is one of the most important basic techniques for making products[1]. Recently, Kunio Mori and coworkers[2-6] have proposed a new molecular junction technique which connects via chemical bonds using a molecular joining agent in place of the conventional adhesion junction technique using adhesives which is based on the principle of wettability. The molecular junction technique which operates by using molecular joining agents has very high reliability because its principle is based on the formation of chemical interfacial bonds, forming a joint between different materials with a molecule at the interfaces. The molecular joining agents are chemical compounds having two type of functional groups which do not react with each other, for example including a combination of a thiol group and an ethoxysilyl group.

In the molecular junction technique between metals and epoxide adhesives using 6-(3-triethoxysilylpropylamino)-1,3,5-triazine-2,4-dithiol-monosodium salt (TES) as the molecular joining agent, it is important to understand which of the thiol groups and/or ethoxysilyl groups react with the metal surfaces. In this paper, the reaction of TES with metal surfaces is investigated to understand the relations between the amount of TES and reaction temperature, between the types and the amount of functional groups for S_{2p} and Si_{2p} peaks in XPS surface analysis, and between the type of functional groups and the reaction temperature.

2. Experimental

2.1 Materials and reagents

Ti, Al, Fe, and Sn metals were supplied by The Nilaco Corporation as materials for research. TES was bought from Sulfur Chemical Incorporated. Others were obtained as reagent grades.

2.2 Surface treatment of metals

$20 \times 10 \times 0.1$ mm plates of Ti, Al, Fe, and Sn metal were washed by ultrasonic cleaning in acetone for 15 min at 20 ˚C and then, in addition, were cleaned by corona discharge treatment (11 kV, 6 times, corona master and corona scanner made by Shinko Electric & Instrumentation Co., Ltd., Osaka, Japan). The purified metal plates were immersed in 0.1 wt%-TES alcohol solution (EtOH 95%/H_2O 5%) for 5 min at 20 ˚C and were dried by hair dryer after removal from the solution to give TES-adsorbed metal plates. Then the TES-adsorbed metal plates were heated for 10 min at 25 - 200 ˚C and the unreacted TES was removed from the samples under ultrasonic cleaning in ethanol for 10 min at 20 ˚C to give TES-linked metal plates.

2.3 Measurement

Metal plates after and before surface treatment were measured for surface elements and functional groups by X-ray photoelectron spectroscopy (XPS, ULVACPHI Co., Ltd PERKIN ELMER PHI 5600 ESCA SYSTEM, X-ray; Monochromated AlKα, 1000×1000 μm^2 analytical area, 45 ˚ photoemission angle, C_{1s} = 284.6 eV, 3.0×10^{-8} torr vacuum).