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Formation of a metal/epoxy resin interface

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Abstract

Interfaces between cross-linked polymers and metals play a significant role in fields like splicing and coating, metallization of plastics, microelectronics, micro system technology and nanotechnology. In this paper, we present investigations on the interface formation due to metallization (Au, Ag, Cu and Al) by evapouration of the highly cured epoxy resin system diglycidilether of bisphenol a (DGEBA)–diethylene triamine (DETA) with the focus on the structure formation at the interface. A combination of X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), atomic force microscopy (AFM) and a radiotracer technique was used to analyze the metal/epoxy interface. While a strong metal/epoxy interaction was found for Al, the noble metals Au, Ag and Cu grow in a Volmer–Weber mode due to an interplay of surface diffusion and metal cluster growth. Nevertheless, polymer bulk diffusion of these metals is negligible.

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Keywords: Metallization; Polymer surface; Epoxy; Diffusion; Condensation; Nanoparticles

1. Introduction

Understanding the mechanisms in the interface between technically relevant cross-linked polymers and metals is highly important in many innovative technological fields. Investigations on the interface formation due to metallization (Au, Ag, Cu and Al) of the highly cured epoxy resin system diglycidilether of bisphenol a (DGEBA)–diethylene triamine (DETA) are presented in this paper with the focus on structure formation at the interface (see Fig. 1). A combination of X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), atomic force microscopy (AFM) and a radiotracer technique was used to analyze the metal/epoxy interface.

During metallization, metal is deposited on solid polymer surfaces in atomic form by physical vapour phase deposition. Partly radioactive Ag (Ag-110m) is used for the radiotracer experiments.

Concerning metallization of epoxy resins with noble metals, patent specifications can be dominantly found for epoxy resins as substrate materials for metal

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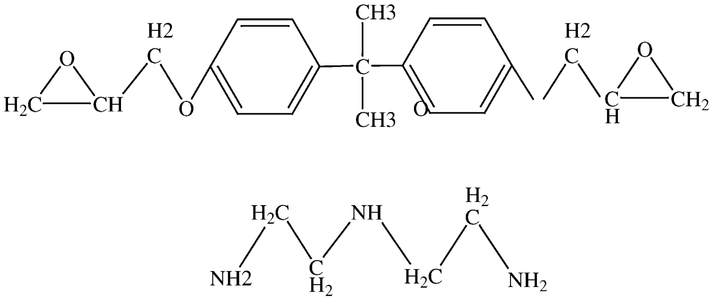

Fig. 1. Diglycidilether of bisphenol A (DGEBA) and diethylene triamine (DETA) molecules.

layers, e.g., in the electrical industry and in the form of lacquers as coatings for metallizations. However, only few investigations on interface interactions can be found in literature, mainly performed on other polymeric substrates [1].

CVD of trimethylaluminum on fluorinepolymers investigated with XPS causes a formation of a stable aluminum oxide layer under the influence of "physisorbed" water. It interacts with the substrate through Al–C bonds [2]. Evapourated aluminum layers on corona treated PET substrates gives rise to a reaction of Al with (C=O) and (C–O) groups of the surface, and the formation of cyclic AlOC complexes [3].

The expected selectivity of the adhesive interaction due to metallization is confirmed phenomenologically. Evapourated Cu layers show good adhesion properties on roughened polypropylene layers and plasma polymerized acrylic acid films whereas, the adhesion strength of polythiophene is by far lower [4]. Furthermore, a diffusion of evapourated Cu, Au and Ag into the near-surface region of different polymers is reported [1,5–9].

For our investigations, the epoxy resin components are mixed at 55 °C for 5 min to exceed the melting point of DGEBA at 42 °C. After rapid cooling further stirring is performed before the curing compound is poured onto a Si wafer. Subsequently, it is kept at room temperature (RT) in a dry CO_2-free atmosphere for at least 48 h. The RT curing is known to be dominated by the cross-linking reactions between oxirane rings of the DGEBA molecules and DETA primary and secondary amine groups (see Fig. 2).

Though the epoxy resin system is in a glassy, well cross-linked state at this preparation stage, the oxirane conversion is far from being completed. As a next step of preparation, the samples are heated up to 120 °C at 10 K/min (starting point of the post curing process). In addition to the above-mentioned cross-linking reactions (see Fig. 2), secondary cross-linking reactions with higher activation energies could take place between oxirane groups and hydroxy groups, which were built during the reactions between oxirane and amine groups. However, this reaction is quite slow even at elevated temperatures and the much more reactive amine groups should dominate the post curing for systems with excess DETA amine hydrogen in comparison to the amount of DGEBA oxirane groups. The "model system" contains a mass ratio of 100:14 between DGEBA and DETA components, which reflects a slight excess amount of amine hydrogen in comparison to oxirane groups, as frequently encountered in technical applications. This system reaches a total oxirane conversion of less than 75% after 48 h of RT curing [10]. Additional post curing for 1 h at 120 °C makes the system reach a quite brittle state with a glass transition temperature of (131 ± 3)°C ($T_{g,\mathrm{midpoint}}$ DSC at a heating rate of 10 K/min).

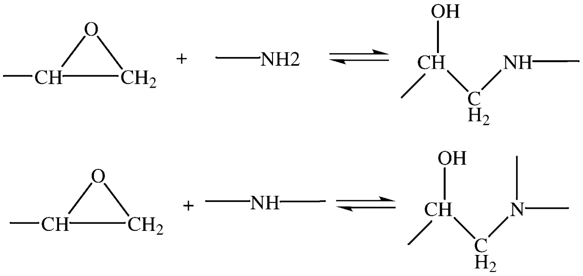

Fig. 2. Cross-linking reactions between oxirane rings of the DGEBA molecules and DETA primary and secondary amine groups.