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Analysis of molecular morphology and permeation behavior of polyimide-siloxane molecular composites for their possible coatings application

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Abstract

This study investigates two different molecular composite coatings (MCCs). All the components as well as compositions constituting each MCC were synthesized and characterized employing different analytical techniques. Studies of the surface morphology of the MCCs have shown heterogeneous distribution and phase separation in coatings. Theoretically calculated Gibbs free energy of mixing showed that phase separation in MCCs occurred with the increase in concentration of the minor component in major one. Different types of domain morphologies have been revealed and the probable mechanism of their formation has been detailed. An understanding of the absorption and hence percolation of water molecule through the succeeding layers of MCCs has been developed. Various factors governing the diffusional phenomenon has been studied and correlated with the underlying phase separated microstructures of MCCs.

Keywords: Polysiloxane; Polyimide; Anti-corrosive coatings; Morphology; Water absorption

1. Introduction

Degradation of metal surfaces due to corrosion is a serious problem in microelectronics, aerospace as well as civil and defense sectors. In microelectronics, for example, corrosion leads to a loss of surface conductivity, deterioration of components, and an increase in contact resistance [1]. The reliability of a metal is normally based on its ability to resist corrosion. Organic and inorganic chromate conversion coatings are applied to metal surfaces that are susceptible to corrosion because they inhibit corrosion. However, the Environmental Protection Agency (EPA) objects to their use because they are carcinogenic [2]. Therefore, there is a strong need for new materials that can serve as effective corrosion barriers for metals. Corrosion phenomena on a coated metal surface are governed by processes such as migration of ionic and non-ionic species through the coating to the coating-metal interface as well as adhesion of the coating to the surface. Diffusion of moisture can lead to a change in the matrix's composition, which results in the delamination of the coating [3]. Thus, the performance of a coated metal substrate depends largely on the composition of the substrate, the composition and thickness of the coating, the interfacial adhesion, and the environment to which the coated substrate is exposed.

Multiphase polymeric systems, rubber like phase and their rigid, glassy or crystalline component may make them an effective anti-corrosion and anti-abrasion material. However, the underlying advantages can be obtained only when the properties of the phases (their morphologies) and the interphase between the two components are carefully controlled and manipulated. Most of the binary pairs form an immiscible system with high positive free energy of mixing. In the field of coatings technology, polysiloxane has been utilized as candidate material to meet specific requirements [4,5]. Similarly, polyimide (PI) has been studied and used in corrosion protection of metals [6–9]. In spite of numerous advantages, including excellent planarization characteristics and the ability to form a defect free film, there are potential problems associated with PI, the foremost being that it is moisture sensitive and not impervious to moisture ingress, a weakness that can lead to the formation of hydrated inorganic-polymer interfaces (a corrosion product) and subsequent delimitation and coating failure. Thus, the subject of

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water transport in organic coatings such as PI has been a field of considerable research [10]. There are no conclusive answers to questions such as how much water can enter the polymer structure, where it resides, how it interacts with the polymer chains, and how it affects the properties of the resultant coatings. On the other hand, polysiloxane is known for its good adhesion and ability to repel water. The hygroscopic nature of PI can be minimized by introducing polysiloxane without losing its core properties. In this paper, we discuss polyimide-siloxane based molecular composite coatings, their water absorption behavior, and the correlation of absorption process with the inherent micro-structural morphology.

2. Methods

Analytical grade benzene-1,2,4,5-tetracarboxylic-1,2,4,5-dianhydride and 4,4′-diaminodiphenyl ether were supplied by Merck Chemical Company. Analytical grade tetrahydrofuran (THF) and *N*,*N*′-dimethylacetamide (DMAC) were supplied by Aldrich Chemical Company and were purified by distillation under reduced pressure and dried over calcium hydride for 24 h. Analytical grade (99.7% pure) dimethyldichlorosilane and dichloreophenylmethylsilane were supplied by Across Chemical Ltd. Deionized, double-distilled water was used in this study.

Polyamic acid was prepared as reported elsewhere [11]. The amount of 0.05 mole of 4,4′-diaminodiphenyl ether (ODA) in 188 g of dry DMAC was placed in a 500-ml three-necked round-bottom flask fitted with a mechanical stirrer, nitrogen inlet, and drying tube of $CaCl_2$. An amount of 0.05 mole benzene-1,2,4,5-tetracarboxylic-1,2,4,5-dianhydride (PMDA) was slowly added to the solution and then vigorously mixed. The mixture was stirred for an additional 2 h in a nitrogen atmosphere. The concentration of solution was 10% and had an intrinsic viscosity of 9.37 dl/g at 26 °C when stored at −10 °C.

Polydimethylsiloxane (PDMS) was synthesized by dropwise additions of 25 ml dimethyldichlorosilane to the saturated aqueous solution of NaCl in a three-necked round-bottom flask fitted with a nitrogen inlet, water condenser, and magnetic stirrer. The temperature of the reaction was kept to approximately 2 °C during the entire process. Products obtained after hydrolysis were extracted with diethylether, washed several times with water, and then washed with a diluted solution of $NaHCO_3$ to remove the last traces of acid. The resultant polymer was transparent and had a low intrinsic viscosity of 12.13 dl/g and a density of 0.96 g/ml.

Polymethylphenylsiloxane (PMPS) was synthesized by the hydrolysis of 25 ml dichlorophenylmethylsilane with ice-chilled water (∼2 °C) in a three-necked round-bottom flask equipped with a nitrogen inlet, water condenser, and magnetic stirrer. The resulting viscous oily layers were extracted with diethylether, washed several times with water, and then washed with a very dilute solution of $NaHCO_3$ to remove the last traces of acid. A transparent, low viscous polymer with an intrinsic viscosity of 13.14 dl/g and a density of 0.97 g/ml was obtained.

In order to prepare coatings, various concentrations of PDMS and PMPS were taken in a known volume of tetrahydofuron and added to a fixed quantity of polyamic acid (PAA) to produce the molecular composite coating (MCC) of required concentrations. These coatings were designated as polydimethylsiloxane-imide (DMSI) and polymethylphenylsiloxane-imide (PMSI) 1, 3, 5, 10, and 15, respectively, where numerals denote the percentage of polysiloxanes in the MCCs. THF was chosen as a solvent because of its miscibility with DMAC and its use as a solvent for the preparation of PAA. Additionally, it was also necessary to ensure that the two solvents not interact with each other. Various MCC compositions comprising two polymers were prepared by mixing them for 2 h with a propeller rotating in a flask at 200 rpm in a flowing nitrogen atmosphere. Using a doctor's blade to ensure uniform thickness of 25 ± 2 μm to meet ASTM-D570 [12], measured quantities of different MCC compositions were spread over a clean, dry glass plate in a dust free chamber. The coatings on the glass plate were kept overnight at ∼50 °C after which they were slowly heated to 350 °C. Coatings were then cooled to room temperature and removed from the glass plate.

3. Characterization

Carbon (^{13}C) nuclear magnetic resonance (NMR) was carried out on a Bruker 400 MHz instrument in $CDCl_3$ as solvent. All the $CDCl_3$ spectra were referenced to tetramethylsilane. Size exclusion chromatograms (SECs) were obtained as reported previously [13] on a high performance liquid chromatography setup from Wyatt Technology Inc. using ASTRA® Software. A column used for the purpose was mixed beads 300 mm × 8 mm SDV with approximately 1×10^2–3×10^6 g/mol separation range. Toluene was taken as a mobile phase for the analysis. Fourier transformation infrared spectroscopic (FTIR) images and corresponding spectra of thin coatings were taken on a Thermo Nicolet Nexus 670 FTIR instrument with a Continuum microscope and Omnic/Atlus software. For surface micro-morphological studies, samples were coated with carbon and studied using a Jeol 5900 LV scanning electron microscope (SEM) and CAMECA SX50 electron probe microscope (EPM) with an energy dispersive X-ray analysis (EDXA) attachment.

4. Monitoring the transport properties

Different compositions of MCCs were extracted with methanol in order to remove hydrogen bonded DMAC from coatings because it remains associated even after the complete imidization of a PI MCC. The extractions from the weighed coatings were continued for 48 h followed by vacuum drying the samples at 70 °C for 24 h. Dried samples were weighed on a model AD4 Perkin-Elmer microbalance and then dipped in deionized double-distilled water. The results were compared with the same studies on controlled samples of polyimide. The percentage of water absorbed was calculated as

$$\text{Water}\,(\%) = \frac{W_\text{f} - W_\text{i}}{W_\text{i}} \times 100 \quad (1)$$

where W_i and W_f are initial and final weights of the coatings.