



Full length article

Molecular design of confined organic network hybrids with controlled deformation rate sensitivity and moisture resistance



Yichuan Ding, Qiran Xiao, Reinhold H. Dauskardt*

Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305-2205, USA

ARTICLE INFO

Article history:

Received 4 July 2017

Received in revised form

26 September 2017

Accepted 26 September 2017

Available online 26 September 2017

Keywords:

Environmental assisted cracking

Deformation rate sensitivity

Fracture mechanism

Thin film

Composites

ABSTRACT

We demonstrate molecular design strategies for engineering the deformation rate sensitivity and fracture resistance of organic-inorganic hybrid films in moist environment. Hybrids with intimate mixing of inorganic and organic molecular networks were synthesized with an epoxy-functionalized silane, (3-glycidoxypropyl) trimethoxysilane and an acetate-stabilized zirconium alkoxide, tetra-n-propoxyzirconium. The highly confined non-hydrolysable organic molecular network connectivity was systematically manipulated by tuning the epoxy ring opening polymerization reaction and the incorporation of carbon bridges of selected lengths. By investigating the corresponding time-dependent crack growth in moist environments, new insights into the fundamental molecular-scale relaxation and cracking mechanisms of the hybrids are provided. These processes were found to be impacted by the confined organic network connectivity which results in significant changes in the deformation rate sensitivity and fracture resistance. With increasing non-hydrolysable organic network connectivity, mechanical behavior that varied from almost perfectly elastic to increasingly viscoelastic could be obtained in a controlled fashion. The related resistance to cracking in moist environments was found to be significantly improved. These findings provide a basis for the rational design of functional hybrids with precisely defined mechanical properties.

© 2017 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

We focused on the molecular design of organic-inorganic hybrids with controlled deformation rate sensitivity and fracture resistance in moist environment. Intimate mixing of organic and inorganic molecular components provides opportunities for modulating the confined non-hydrolysable organic molecular networks to achieve selected properties. Using a time-dependent crack growth study, the molecular-scale relaxation and crack-growth mechanisms are quantitatively explained using a model in which the synergistic behavior of the organic and inorganic molecular networks are highlighted.

Hybrid films comprising an inorganic molecular network formed via a condensation reaction after hydrolyzation, and an organic molecular network formed by ring opening polymerization were synthesized with an epoxy-functionalized silane, (3-glycidoxypropyl) trimethoxysilane (GPTMS), and an acetate-

stabilized zirconium alkoxide, tetra-n-propoxyzirconium (TPOZ-Ac) [1–3]. The organic network was systematically modulated through tuning the amount of organic network crosslinker, the curing temperature and incorporating dipodal silanes with selected carbon bridge lengths. X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) were utilized for assisting in elucidating the chemical structure changes happened in the molecular-scale.

Deformation rate sensitivity and fracture resistance were measured using time-dependent crack growth in moist environments. While often quantified by the critical fracture energy, G_c (J/m²), crack growth can occur at significantly lower loads when reactive environmental species, like moisture, are present [4–11]. This phenomenon, referred to as environmental-assisted cracking, involves the synergistic effect of mechanical stress and the environmental species. This time-dependent crack growth process can be used to provide insight into the fundamental molecular-scale relaxation mechanisms and crack-growth kinetics which are linked to the viscoelasticity and fracture resistance.

In this study, the crack growth kinetics which describe the crack growth rates as a function of the applied debond driving force G

* Corresponding author. Durand Bldg., Rm. 121, Stanford University, Stanford, CA 94305-2205, USA.

E-mail address: dauskardt@stanford.edu (R.H. Dauskardt).

over the range of $\sim 5 \times 10^{-4}$ to $\sim 5 \times 10^{-9}$ m/s were measured. Using a moisture transport and a viscoelastic relaxation model, the crack growth kinetics were quantitatively explained in terms of the deformation rate sensitivity and fracture resistance. They were found to be affected by the confined organic network within the hybrid. With increasing non-hydrolysable organic network connectivity, the mechanical behavior of the hybrids varied from almost perfectly elastic to increasingly viscoelastic in a controlled fashion. The related fracture resistance was found to be significantly improved. These findings provide a basis for the rational design of design functional hybrids with precisely defined mechanical properties.

2. Experimental methods

2.1. Sol-gel precursors preparation

(3-Glycidoxypropyl)trimethoxysilane (GPTMS, 98%, Sigma-Aldrich Co., Madison, WI), (3-glycidoxypropyl)methyldimethoxysilane (GPMDMS, 96%, VWR international LLC, Radnor, PA), methyloxypropyltrimethoxysilane (MPTMS, 98%, Gelest Inc., Morrisville, PA), bis(triethoxysilyl)methane (BTESM, 99%, Gelest Inc., Morrisville, PA), 1,2-bis(triethoxysilyl)ethane (BTESE, 99%, Gelest Inc., Morrisville, PA), 1,6-bis(trimethoxysilyl)hexane (BTMSH, 99%, Gelest Inc., Morrisville, PA), tetra-*n*-propoxyzirconium (TPOZ, 70% in *n*-propyl alcohol, Sigma-Aldrich Co., Madison, WI), and glacial acetic acid (GAA, EMD, Gibbstown, NJ) were used as received. The chemical structures of these precursors are summarized in Fig. 1.

3.75 wt% GPTMS in water and TPOZ-Ac (TPOZ stabilized with 45 wt % GAA) in water were used as two precursors for making the reference film. Both solutions were aged with continuously stirring at 500 rpm for 24 h.

To study the interrelationship between the hydrolysable inorganic molecular network and time-dependent moisture-assisted crack growth of the hybrid film, we adjusted the level of inorganic connectivity by replacing one of the precursors, GPTMS (0 methyl group) solution, by GPMDMS (1 methyl group) solution while maintain all the other experimental parameters the same. Inorganic network connectivity is expected to decrease since methyl group cannot hydrolyze and condense to form Si–O–Si or Si–O–Zr inorganic networks.

To study the interrelationship between the non-hydrolysable organic molecular network and time-dependent moisture-assisted crack growth of the hybrid film, we first adjusted the amount of organic crosslinker by partially substituting the GPTMS with MPTMS while keep all other experimental parameters the same. (GPTMS + MPTMS)/water solution with various combinations of GPTMS and MPTMS was used as the precursor together with a TPOZ-Ac/water solution. The MPTMS precursor resembles the GPTMS in that the only difference in MPTMS is the methyl group which replaced the epoxy ring. It is expected that the connectivity of the organic network will decrease as the amount of the organic crosslinker, the epoxy ring, was reduced in the film.

We then incorporated carbon bridges into the film by partially replacing GPTMS with dipodal silanes with different carbon bridge lengths while keeping all other experimental parameters the same. Incorporation of BTESM, BTESE, BTMSH, 3 different dipodal silanes with a 1 carbon atom bridge, a 2 carbon atom bridge, and a 6 carbon atom bridge, were investigated.

All experimental work was carried out in a laboratory air environment, which remained constant at 25 °C and approximately 40–45% relative humidity.

2.2. Film deposition

The hybrid films were deposited onto natively oxidized single crystal [100] silicon substrates ($50 \times 12.5 \times 0.77$ mm) by dry-regime dual-source concurrent spraying reported previously [12]. During spraying, precursor solutions (silane/water and TPOZ-Ac/water) were further diluted with 60 vol% isopropyl alcohol for improving the surface smoothness. Two syringe pumps were each programmed to a constant infusion rate of 0.25 ml/min to separately deliver precursor solutions into a pressurized nozzle where liquid was atomized and sprayed onto the substrate. More details can be found elsewhere [12] and the final film thickness was ~ 135 nm without any holes or empty spots.

2.3. Specimen preparation

Following the film drying in air at 60 °C for 10 min, double cantilever beam (DCB) specimens were prepared by sandwiching two spray coated silicon substrates with approximately 5 μ m thick highly cross-linked brittle epoxy resin in between. The DCB specimens were then thermally cured for 2 h at 160 °C in air unless stated otherwise.

2.4. Time-dependent crack growth in moist environments

To study the time-dependent crack growth of the hybrid film in moist environments, the testing system was placed in a controlled environment at constant temperature (± 1 °C) and RH ($\pm 2\%$ RH) followed by a 12 h equilibration period. DCB specimens were loaded to just below critical point at which the displacement was fixed. The rate of load relaxation that resulted from crack extension was measured to determine the crack growth velocity. Detailed calculation procedures have been described elsewhere [4,13]. Moisture-assisted crack growth velocities were characterized as a function of the applied debond driving force G over the range of $\sim 5 \times 10^{-4}$ to $\sim 5 \times 10^{-9}$ m/s to produce a characteristic da/dt versus G curve. The deformation rate sensitivity was determined by fitting the da/dt versus G curve based on the proposed model discussed in the following sections. At least two separate sets of samples were measured for each test to ensure reproducibility. In this work, all measurements were conducted at 85% RH and 25 °C.

2.5. Film composition and delamination pathway characterization

XPS (PHI 5000 Versaprobe system, ULVAC-PHI Inc., Chanhassen, MN) was employed to analyze the chemical composition of the as-deposited films. Together with high resolution optical microscopy, XPS was also used to determine the debond pathway in the film structure. The chemical structures in the coating were characterized using ATR-FTIR (Nicolet iS50, Thermo Fisher Scientific, Waltham, MA).

3. Results and discussion

3.1. Time-dependent crack growth mechanisms of the hybrid film

The time-dependent moisture-assisted crack-growth curve for the reference organic-inorganic hybrid film made of GPTMS and TPOZ is shown in Fig. 2(a) where fracture occurred cohesively within the hybrid film. Unlike the curves typically seen in bulk glasses and thin silica films, the curve here clearly exhibiting 3 unusual regimes, namely a weak G dependent regime at $da/dt > \sim 10^{-5}$ m/s (Region A), a strong G -dependent regime over the range from $\sim 10^{-5}$ to $\sim 10^{-8}$ m/s (Region B), and a weak G dependent regime below $\sim 10^{-8}$ m/s (Region C). Weak G dependent plateau

Download English Version:

<https://daneshyari.com/en/article/5435701>

Download Persian Version:

<https://daneshyari.com/article/5435701>

[Daneshyari.com](https://daneshyari.com)