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# Hybrid coatings from novel silane-modified glycidyl carbamate resins and amine crosslinkers

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ABSTRACT

Organic–inorganic hybrid coatings were prepared using silane-modified glycidyl carbamate resins and different amine crosslinkers via the sol–gel process. Two different silane-modified glycidyl carbamate resins with 33% and 20% silane modification were prepared. The synthesized resins were crosslinked with amine crosslinkers such as Amicure PACM, Ancamide 805, Ancamide 2050, Ancamide 2353, Epicure 3164, Jeffamine D-400, etc., at different epoxy to amine equivalent ratios. The formulated hybrid coatings were cured at laboratory temperature and humidity for more than 20 days and subjected to different tests. The hybrid coatings were analyzed using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) during network maturation. Post-cured coatings were also analyzed to understand the effect of structural variables on the coatings thermal properties. Mechanical testing of the post-cured coatings such as König pendulum hardness, crosshatch adhesion and impact resistance were also evaluated. Solvent resistance of the coatings was evaluated by of testing the methyl ethyl ketone (MEK) double rub resistance. Atomic force microscopy (AFM) was used to characterize the surface topography of the hybrid coatings. Finally, structure–property correlations were given based on the observed results.

## 1. Introduction

The interest in developing novel organic–inorganic (O–I) hybrid coatings in recent years is due to the unique properties derived from combining inorganic and organic components into a single coating system. Sol–gel chemistry provides an easy, cost-effective and efficient way to incorporate inorganic components into an organic binder. Incorporation of inorganic silica networks into organic binders and producing the O–I hybrid materials have been extensively studied because they can exhibit a wide range of improved multifunctional properties, including toughness, impact strength, tensile strength and thermal stability. When properly formulated, this technology produces transparent, hard and stable coatings with improved thermo-mechanical properties suitable as abrasion resistant materials [1–14]. O–I hybrid materials can be easily prepared at room temperature using the sol–gel process. The inorganic phase is obtained from hydrolysis and condensation reactions in the sol–gel process of metal alkoxides of the type $[(M(OC_nH_{2n+1})_z]$, where M is Si, Ti, Al, Sn, Zr, etc. [15]. O–I hybrid synthesis procedures may involve either (1) sequential polymerization, where the inorganic phase is formed within a preformed organic matrix, or (2) simultaneous polymerization, where both the organic and inorganic networks are formed simultaneously. Hybrids may be formed with or without covalent bonding of the inorganic component to the organic polymer matrix [16]. In the absence of any covalent connection between the organic and inorganic phase, the O–I hybrid is generally phase separated due to the formation of hard silica nano-domains, which often decreases film mechanical properties. The morphology model of O–I networks assumes organic- and inorganic-rich phases as well as a mixed interphase [17]. According to Wilkes' morphological model, a silica based O–I hybrid is a polymer-rich matrix with dispersed silica-rich domains and a mixed phase of partly condensed siloxane clusters and an organic polymer [18]. A finely dispersed silica phase can act as a polymer filler and inhomogeneities of various sizes may be formed [19]. In order to achieve an optimum balance of properties, formulators should avoid phase separation between the soft and hard components of such system. A general approach to increase the crosslink density and thus obtain stronger interfacial interactions between the inorganic and organic components is to use silica coupling agents as crosslinkers. These can react with functional groups present on the polymer molecules or they can crosslink by reaction with an added multifunctional molecule. The functional group present in the coupling agent establishes a bridge between the organic and inorganic components; thus well-dispersed nanostructured phases may result [20]. In order

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to achieve homogeneous phase morphologies, the inorganic and organic networks are formed together (often simultaneously) [21]. In this way, a predetermined structure and morphology of the O–I networks connected to a set of material properties can be custom-tailored by manipulating reaction conditions during synthesis or by using precursors of various molecular architectures.

Webster et al. have prepared glycidyl carbamate (GC) resins, biuret glycidyl carbamate (BGC) and isocyanurate glycidyl carbamate (IGC), from hexamethylene disocyanate biuret (HDB) and hexamethylene disocyanate trimer (HDT), respectively [22,23]. BGC and IGC resins have the advantage of combining PU and epoxy properties into a single system. Additionally, the incorporation of silica nanostructures via the sol–gel route in the GC resin will produce GC-silica hybrid networks that not only show the properties of carbamate linkages and epoxy-amine thermosetting system but also possess the benefits of the O–I hybrid structure. For GC-silica hybrid coatings, the silane network-former 3-aminopropyl trimethoxysilane (APTMS) establishes chemical linkages between the inorganic silica network and the organic polymeric network. APTMS can be utilized in two different ways in order to form the GC-silane hybrid coatings. First, the $-NH_2$ group of APTMS can be reacted with the available epoxy groups of IGC or BGC resin, followed by sol–gel hydrolysis–condensation reaction of the reactive tri-methoxy groups bonded to the Si atom. Second, the NCO groups of HDB or HDT can be partly reacted with APTMS and then the remaining NCO groups can be reacted with glycidol, so that one can synthesize a silane-modified GC resin. The obtained silane-modified GC resins can be used to formulate hybrid coatings using the sol–gel hydrolysis–condensation reaction of the reactive tri-methoxy groups bonded to the Si atom in the silane-modified GC resin. The first methodology of synthesizing GC-silica hybrid coatings and their property evaluation is reported elsewhere [24], whereas the present study describes the second method of obtaining GC-silica hybrid coatings using amine crosslinkers. Amine crosslinkers such as *p*-aminocyclohexyl methane (PACM), Ancamide 805 (A805), Ancamide 2050 (A2050), Ancamide 2353 (A2353), Epicure 3164 (E3164), Jeffamine D-400 (J400) and Jeffamine D-2000 (J2000) were used to crosslink the available epoxy groups in the silane-modified GC resin prepared from HDB. The hybrid coatings were characterized using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Coating mechanical properties such as König pendulum hardness, impact resistance and adhesion were determined.

## 2. Experimental

### 2.1. Materials

Glycidol was provided by Dixie Chemical (Houston, Texas) and stored in a refrigerator until the reaction was carried out. Tolonate HDB-LV (HDB) was kindly supplied by Rhodia Inc. 3-Aminopropyl trimethoxysilane (APTMS), dibutyltin dilaurate (DBTDL), methyl ethyl ketone (MEK), ethyl 3-ethoxyethyl propionate (EEP) and 4 Å molecular sieves were purchased from Aldrich (Milwaukee, WI). *tert*-Butyl acetate (TBA) was supplied by Ashland Distribution Co (Columbus, OH). Crosslinkers such as Amicure PACM (bis(*p*-aminocyclohexyl) methane), Ancamide 805 (100% reactive polyamide, equivalent weight per [H] is 124), Ancamide 2050 (polyamine adduct; equivalent weight per [H] is 150) and Ancamide 2353 (modified polyamide; equivalent weight per [H] is 114) were kindly supplied by Air Products and Chemicals, Inc. (Allentown, PA). Jeffamine D-400 (amine hydrogen equivalent weight of 115) and Jeffamine D-2000 (amine hydrogen equivalent weight of 514) are diamine-terminated polypropylene oxides, kindly supplied by Huntsman Chemicals (Conroe, TX). Epicure 3164 (oligomeric polyamine; amine hydrogen equivalent weight of 256), a product of Hexion, was obtained from Miller-Stephenson Chemical Company, Inc (Connecticut, USA). Solvents were freed from moisture using 4 Å molecular sieves before use.

### 2.2. Synthesis of silane-modified GC resin

The required amount of HDB was weighed into a reaction kettle. The kettle was equipped with a mechanical stirrer, addition funnel and a thermocouple to record the temperature. At room temperature, part of the available NCO groups in HDB was reacted with APTMS by a slow addition of APTMS through an addition funnel (step I; Scheme 1). Following completion of the reaction with APTMS, the remaining unreacted NCO groups were reacted with glycidol at 45–55 °C (step II; Scheme 1). The reaction in step II was continued until the complete disappearance of the NCO peak at 2270 $cm^{-1}$ in the FTIR spectrum was observed. In this way, 20% and 33% silane-modified GC resins BGC20Si (solid content: 88.4 wt.%) and BGC33Si (solid content: 86.5 wt.%), respectively, were prepared in different solvents such as TBA and EEP. The synthesized silane-modified GC resins were stored in glass bottles.

### 2.3. Formulation of coatings from silane-modified GC resin and amine crosslinkers

The silane-modified GC resins were mixed with an appropriate amount of the amine crosslinker, such as PACM, A805, A2050, A2353, E3164, J400 and JD2000, and cast on glass and sanded Al-2024 panels using a draw-down bar having an 8 mil gap. The epoxy equivalent of silane-modified GC resins and amine equivalent of crosslinker were varied to study their effect. Formulated hybrid coatings were kept at laboratory temperature and humidity for more than 20 days for network maturation. Table 1 shows the sample name and compositions of the hybrid coatings prepared from

**Table 1**
Sample name and compositions of the hybrid coatings.

| Sample name | Resin | Crosslinker | Epoxy (modified GC):amine (crosslinker) | Solvent used during coating formulation |
|---|---|---|---|---|
| C3A805$_t$-1 | BGC33%Si | A805 | 1:1 | TBA |
| C3A2050$_t$-1 | | A2050 | | |
| C3A2353$_t$-1 | | A2353 | | |
| C3E3164$_t$-1 | | E3164 | | |
| C3PACM$_t$-1 | | PACM | | |
| C3PACM$_t$-2 | | PACM | 1:2 | |
| C3A805$_e$-1 | | A805 | 1:1 | EEP |
| C3A2050$_e$-1 | | A2050 | | |
| C3A2353$_e$-1 | | A2353 | | |
| C3E3164$_e$-1 | | E3164 | | |
| C3PACM$_e$-1 | | PACM | | |
| C3PACM$_e$-2 | | PACM | 1:2 | |
| C3J400$_e$-1 | | J400 | 1:1 | |
| C2A805$_t$-0.5 | BGC20%Si | A805 | 1:0.5 | TBA |
| C2A2050$_t$-0.5 | | A2050 | | |
| C2A2353$_t$-0.5 | | A2353 | | |
| C2E3164$_t$-0.5 | | E3164 | | |
| C2A805$_t$-1 | | A805 | 1:1 | |
| C2A2050$_t$-1 | | A2050 | | |
| C2A2353$_t$-1 | | A2353 | | |
| C2E3164$_t$-1 | | E3164 | | |
| C2PACM$_t$-1 | | PACM | | |
| C2J400$_t$-1 | | J400 | | |
| C2A805$_t$-1.8 | | A805 | 1:1.8 | |
| C2A2050$_t$-1.8 | | A2050 | | |
| C2A2353$_t$-1.8 | | A2353 | | |
| C2E3164$_t$-1.8 | | E3164 | | |
| C2PACM$_t$-1.8 | | PACM | | |
| C2J400$_t$-1.8 | | J400 | | |
| C2J2000$_t$-1.8 | | J2000 | | |