



Click-based transparent durable films derived from tetrabrachius PDMS-bridged epoxy acrylates and surface modified nanosilica particles



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ABSTRACT

We propose a novel tetra-arm polydimethylsiloxane-bridged aryl-ether-functional epoxy acrylate (EAAE-PDMS), which was employed as a precursor to crosslink with systematic variations (0, 1, 3, 5, 15 wt.%) of thiol-functionalized silica nanoparticles (SNs) through a thiol-ene click chemistry, resulting in transparent hybrid films (EAAE-PDMS/SiO₂). The unique tetrabrachius structure of EAAE-PDMS can result in significantly high cross-linking densities and high gel content of their thermosets. The introduction of PDMS bridge in the precursor backbone and the modification of SNs are simultaneously in favor of better compatibility between the organic/inorganic components, benefiting for the distinctly improved surface mechanical properties namely scratch hardness and abrasion resistance relative to common epoxy acrylates. A sound proof is the fact that either our hybrid film derived from neat EAAE-PDMS or its mixture with thiol-functionalized SNs shows an increased 5%-mass-loss temperature at least by 90 °C and up to 7-fold enhancement in the abrasion resistance relative to the silica-free EA film. Finally, the as-made films show excellent solvent and thermal resistance and strong adhesion, providing strong potentials for application in dielectric and mechanic materials.

1. Introduction

High performance organic thin films are much sought after for high-added-value applications such as sensors, optic-electronics and mechanics. For most ultrathin films, they are frequently subjected to mechanical abrasion during their normal use. Another important point is that most films composed of polymeric components such as paints, typically require a thickness in the micrometer range to be mechanically robust or to have a reasonable scratch resistance [1,2]. Unfortunately, any film totally or partially composed of organic or polymeric constituents often lacks sufficient mechanical robustness and durability, relative to its inorganic counterparts. Incorporation of inorganic nanoparticles (INs) in an organic host matrix appears to be effective in addressing these shortcomings [3]. The resultant nanocomposites are intended to combine the popularity of polymer matrices (low weight, flexibility and easy formability) with the unique features like hardness, scratch and abrasion resistance, and thermal stability of the inorganic fillers [4,5]. However, the tendency of highly polar nanofillers to aggregate and consequently to poorly disperse in the polymer matrix, which leads to certain macroscopic heterogeneity, is detrimental for the nanocomposites final functionality. Additionally, hydrophilic silicon

fillers are expected to exert an unexpected thickening effect in solvent mediums, accounting for limited processability totally useless as coatings.

For achieving a high content of INs filler with easy processability while avoiding certain phase separation, surface modification of the nanofillers proves to be effective. The thiol-ene photo-curing chemistry, proves to be a successful strategy for surface function of inorganic nanoparticles as well as construction of nanoscale hybrid films [6,7]. Its advantages lies in a solvent-free formulation, controllable and faster cure efficiency, and low energy consumption comparing with thermal curing, and also delivers the possibility of curing at room temperature. Besides, due to its step-growth free-radical process thiol-ene photopolymerization can be less sensitive to oxygen than normal radical cure. Drawbacks of other typical photo-initiated radical polymerization processes, i.e. shrinkage and the formation of heterogeneous networks, have also been effectively avoided [8].

Epoxy acrylate resin offers numerous advantages including excellent adhesion, good processability and mechanical strength, and has been widely used in various industrial fields [9–11]. However, the existing drawbacks (i.e. low physic-chemical stability, high water absorption, poor electrical and dielectric properties) damage their

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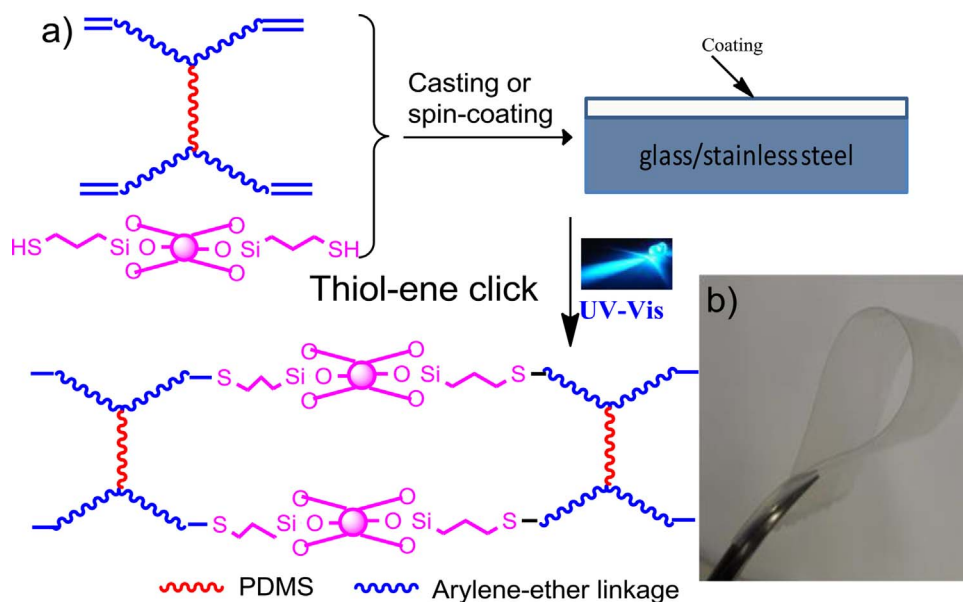


Fig. 1. Proposed curing route for the composite film of EAAE-PDMS.

popularity for extensive utilities as advanced composite matrices in high-tech electronic and optical applications [10]. Recent efforts have been contributed to improve the general performances of films, i.e. enhancing stability, lowering surface energy, promoting dielectric and tribological properties [12–17]. Backbone modification of epoxy acrylate like introduction of rigid-rod aromatic backbones proves to be another effective way, without sacrificing other attracting properties [18]. Poly(aryl ether), in general, are endowed with high glass transition temperatures, excellent thermal and oxidative resistance, outstanding mechanical properties, and extraordinary corrosion resistance, meeting the rigorous demands for utilities in hot and hostile environments [19,20]. Numerous routes have been established to prove the popularity of molecular designing of novel epoxy acrylate resins functionalized by poly(aryl ether)s [21–23].

As part of an ongoing project dealing with high performance nanocomposites, herein, we present a simple synthetic strategy to build a tetrabrachius polydimethylsiloxane-bridged epoxy acrylate (EAAE-PDMS) and to promote their curing with thiol-functionalized silica nanoparticles (SNs) via simple UV-induced thiol-ene click chemistry (Fig. 1). To the best of our knowledge, the use of such tetra-arm epoxy acrylate as a macromolecular precursor to prepare thermosetting hybrid films has not been reported so far. Indeed, a careful structure-property study of the nanocomposites demonstrated that the tetra-arm PDMS-bridged aryl-ether-functional epoxy acrylate and thiol-modified SNs, ultimately control the curing process and dominate the final performance. Compared with those derived from common epoxy acrylate or pristine SNs, our results reported attractively enhanced physical properties of the as-made composite films.

2. Experimental section

2.1. Synthesis of PDMS-bridged aryl-ether-containing epoxy acrylate (EAAE-PDMS)

2.1.1. Synthesis of isocyanate-terminated PDMS (NCO-PDMS)

25.024 g (0.1 mol) of diphenyl-methane-diisocyanate dissolved in 30 mL of dry dimethylformamide was charged, followed by the dropwise addition of dihydroxyl-terminated polydimethylsiloxane (DIOL-PDMS, 0.05 mol, $M_n = 1000$, ESI† for details) at 35 °C. Then the reaction mixture was heated to 65 °C for a period of 1 h with stirring under dried N_2 atmosphere to obtain a NCO-terminated polydimethylsiloxane (NCO-PDMS, Yield 90%). FT-IR(KBr, cm^{-1}): 3295 (N–H), 3316 (N–H), 1736 (C=O), 1600(Ar–H), 1591(Ar–H), 770.

2.1.2. Synthesis of EAAE-PDMS

To a solution of NCO-PDMS (0.05 mol), 0.1 mol of epoxy-terminated aryl-ether methanol oligomer (simplified as EPEH) in 30 mL of dry dimethylformamide was added dropwise at 25 °C over 1 h. The reaction mixture was then heated to 80 °C for another 4 h and a pale yellow solution of EPEH-PDMS was obtained. To introduce photo-active groups, acrylic acid (stoichiometric ratio of epoxy verse acid: 1:1.05) and 2 wt.% of tetra butylammonium bromide were dropped slowly at 60 °C along with methoxyphenol (0.03 wt.%). The reaction was carried out at 100 °C for about 24 h to obtain a pale yellow EAAE-PDMS (Yield 79%).

2.2. Surface functionalization of silica nanoparticles with (3-mercaptopropyl) trimethoxysilane to thiol-functionalized silica nanoparticles (SH-SiO₂)

Pristine silica nanoparticles (Diameter: 15 nm; BET: 245 m² g⁻¹) were dried at 110 °C in a vacuum oven overnight, and the content of silanol groups on the surface of nanoparticles was estimated by potentiometric titration of sodium hydroxide. After nanoparticles (10 g) were dispersed by sonication in dry toluene, and 20 mL of MPTS was charged in three times, and the mixture was refluxed for 20 h under argon atmosphere. The resultant powder was separated by centrifugation (1600 rpm), and washed several times with toluene to remove the residual MPTS and then dried under vacuum at 110 °C for 5 h (Yield 91%).

2.3. General procedures for film preparation through directly casting or spin-coating

Hybrid films were yielded by directly casting the solution mixture of EAAE-PDMS and systematic variations (1, 3, 5, 15 wt.%) of surface functionalized silica nanoparticles hybrid on clean glass pieces or stainless steels, and then converted into F@EAAE-PDMS-SiO₂ composite film via photo-induced curing free of inert atmosphere. Typically, for preparing F@EAAE-PDMS-SiO₂ (5%), a mixture of EAAE-PDMS and a precalculated amount of surface-functionalized SiO₂ as well as a photoinitiator of Irgacure 819 (1 wt.%) was added into a DMF solution, and then the ultrasonication was applied for 30 min. The resultant mixture was poured and casted in 3 mm (transmittance measuring) and 200 μm (dynamic mechanical analysis and thermomechanical analysis) thick glass plates. The casted samples were irradiated with a 365 nm mercury lamp (Fusion lamp with a light intensity on the surface of the

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