



Synthesis and properties of epoxy-polyurethane/silica nanocomposites by a novel sol method and in-situ solution polymerization route

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ABSTRACT

In this work, a novel nonaqueous sol method for preparing 3-methacryloxypropyltrimethoxysilane modified nano-SiO₂ (MPS-SiO₂) in *N,N*-dimethylformamide (DMF) substituting alcoholic solvents was developed, and epoxy acrylate resins (EA) based on novolac epoxy resin (EP) were prepared. Epoxy acrylate copolymers (EPAC/SiO₂) with core/shell structure were prepared by one-step in-situ solution polymerization of EA, acrylic monomers and a certain amount of modified silica sol as core. Epoxy acrylate based polyurethane composites/SiO₂ (EPUAs/SiO₂) were finally obtained by curing action among as-prepared EPAC/SiO₂, isocyanate and anhydride curing agent. The obtained EA and MPS-SiO₂ were also characterized using Fourier transform infrared spectroscopy (FTIR), ¹H nuclear magnetic resonance spectra (¹H NMR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and surface contact angle analysis (CA). Microstructures of MPS-SiO₂ and EPAC/SiO₂ in DMF were observed by transmission electron microscope (TEM). Furthermore, the influence of MPS-SiO₂ on the properties of EPUAs/SiO₂ including fracture surface morphology, thermal stability, glass transition temperature (*T_g*), tensile strength, elongation at break, cross-linking density, shore hardness, water absorption, etc. were also investigated. The results demonstrate that colloidal MPS-SiO₂ with DMF as solvent can be directly added into polyurethane system and has industrial application value, EPAC/SiO₂ with core-shell morphologies have good individual dispersion in DMF, and incorporating MPS-SiO₂ into EPUAs/SiO₂ greatly enhances physico-chemical properties of EPUAs/SiO₂ composites.

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Introduction

In the past several decades, polyurethanes (PUs) have attracted considerable attention in chemical engineering applications including coatings [1], adhesives [2], inks [3], elastomers [4,5], foams [6,7], etc. PUs are featured by excellent abrasion resistance, chemical etching resistance, flexibility as well as fabrication versatility [8–12]. However, PUs are limited in engineering application by some disadvantage especially its poor resistance to high temperature and medium mechanical performance. A variety of studies have been performed to solve these problems by incorporating heterocyclic or aromatic structures into the PUs backbone to enhance their thermal stability at high temperature [13–16], or incorporating inorganic nanoparticles e.g. SiO₂, TiO₂, CaCO₃, and Al₂O₃

nanoparticles into PUs to improve their thermal stability, mechanical and physical properties [17–23].

Notably, SiO₂ nanoparticles have been widely introduced into polymers including PUs to improve their physico-chemical properties such as the heat resistance, radiation resistance, and electrical properties of polymer materials [24]. Silica particles such as fumed silica and colloidal silica have been frequently incorporated into PUs/SiO₂ composites, however, it is a fact that it's very difficult to redisperse or de-agglomerate fumed silica properly to produce monodispersed nanoparticles in a polymer matrix due to their specific surface area and volume effects. Most colloidal silica particles are prepared by conventional Stöber method. Silica particles are generated by hydrolysis and condensation of TEOS in alcoholic solvents, where spherical silica particles ended with some reactive hydroxyl groups on their surface. Therefore, to solve above-mentioned agglomerate problem, SiO₂ particles can be surface modified to improve its dispersion in solution by silane chemistry. There are two ways to modify the surface of SiO₂

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Table 1
The process conditions of preparing MPS-SiO₂ sol with different diameters.

Samples	TEOS (M)	MPS (M)	NH ₄ OH (M)	H ₂ O (M)	DMF (M)	Temperature (°C)	Particle size (nm)
M1	0.19	0	1.14	1.11	27.36	70	25.8
M2	0.19	0.08	1.14	1.11	27.36	70	32.7
M3	0.19	0.08	1.14	1.11	27.36	50	50.9
M4	0.24	0.10	1.71	1.11	21.89	50	104.0

particles to improve the interfacial interactions between SiO₂ particles and the polymer matrix. The first way is accomplished through surface absorption or reaction with small molecules, such as silane coupling agents, and the second way is based on grafting polymeric molecules through covalent bonding to the hydroxyl groups existing on SiO₂. The advantage of the second procedure over the first lies in the fact that the polymer-grafted SiO₂ can be designed with the desired properties through a proper selection of the species of the grafting monomers and the choice of grafting conditions [25]. However, in PUs system, alcoholic solvents for preparing colloidal polymer-grafted SiO₂ have been indeed limited due to the hydroxyl groups of alcoholic solvents reacting easily with isocyanate groups of pre-polymer or isocyanate curing agent.

In the present work, we try to solve the above problem by substituting alcoholic solvents with DMF solvent. It is also demonstrated that the nonaqueous sol–gel process is a powerful and versatile alternative as compared to the traditional sol–gel process by imposing structure control and reproducibility in a hybrid synthesis [26], especially, the nonaqueous sol–gel technique using DMF solvent provides an improved control over molecular level homogeneity leading to uniform morphologies. This paper starts with modifying nano-SiO₂ in DMF with the nonaqueous sol method, and epoxy acrylate resins (EA) were prepared by ring-opening reaction of novolac epoxy resin (EP) and acrylic acid (AA). Secondly, epoxy acrylate copolymers (EPAC/SiO₂) with core/shell structure were prepared by in-situ solution polymerization of EA and acrylic monomers directly adding a calculated amount of colloidal modified silica as core. EPUAs/SiO₂ composites were finally obtained by curing action among as-prepared EPAC/SiO₂, isocyanate and anhydride curing agent. The influence of MPS-SiO₂ on the properties of EPUAs/SiO₂ including fracture surface morphology, thermal stability, glass transition temperature, tensile strength, elongation at break, cross-linking density, shore hardness, water absorption, etc., were also investigated.

Experimental

Materials

EP (CYDBN240) with epoxide number of 0.57 was supplied by Yueyang Chemical Factory, Hunan Province, PRC. Tetraethoxysilane (TEOS, Si(OC₂H₅)₄), analytically pure, was purchased by Tianjing Fuchen Chemical Reagent Factory. MPS (CH₂C(CH₃)COO(CH₂)₃Si(OCH₃)₃) was purchased from Diamond Advanced Material of Chemical Inc. Curing agents: 1,6-hexamethylene diisocyanate homopolymer (HDI, Desmodur N3390) were supplied from Bayer Chemical Co., Ltd, Germany. Anhydride, anhydrous ethanol, acrylic acid (AA), styrene (ST), butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA), tetramethylammonium bromide (TMAB), azo-bis-isobutyronitrile (AIBN), hydrochloric acid (HCl), ammonia (NH₄OH), *N,N*-dimethylformamide (DMF), *n*-Butyl acetate and 1,4-dioxane were purchased by Aladdin Reagents Co., Ltd.

Preparation of MPS-SiO₂ in DMF

Monodispersed silica sol was synthesized by a modified Stöber method [27]. In a typical experiment, TEOS and DMF were added

dropwise into a mixture of NH₄OH, H₂O and DMF, and stirred at 300 rpm for 24 h. After that, a calculated amount of MPS and DMF were then added dropwise into the above solution in one hour, and stirred continuously for 24 h at a specified temperature to generate MPS-SiO₂ sol in DMF. The process conditions of preparing MPS-SiO₂ sol in detail are illustrated in Table 1.

Synthesis of EA

A calculated amount of EP (containing 0.32 mol epoxy groups) and DMF were added into a 500 mL four-necked round bottom flask equipped with dropping funnels, mechanical stirrer, reflux condenser, and thermometer, and then EP was heated to 80°C in a water bath kettle. The mixture of AA (0.08 mol, epoxy groups: carboxyl group in molar ratio equals to 4:1) and TMAB (1 wt% based on EP mass) were added dropwise into the four-neck flask and stirred at 1000 r/min at 110°C for 5 h. The course of the ring-opening reaction was monitored by measuring the acid value and epoxide value, as determined by ASTM D 4662-08 and ASTM D 1652-04, respectively. The epoxide value, as defined by the number of moles of epoxy groups per 100 g of the substance, was calculated from the epoxide equivalent weight by the following relationship: epoxide value = 100/epoxide equivalent weight. The reaction was terminated and regarded as complete reaction till the acid value reaching below 5 mg KOH/g and the epoxide value reaches the theoretical value.

Preparation of EPAC/SiO₂ by one-step in-situ solution polymerization

MPS-SiO₂ sol in DMF (1 wt%, 3 wt%, and 5 wt% based on acrylic monomers mass, respectively) was sonicated for 30 min and then added into a 250 mL four-necked flask equipped with mechanical stirrer, reflux condenser, and thermometer. Then acrylic monomers (the mass ratio of ST/BA/HEMA/EA equals to 22/9/6.9/8.5), and 2 wt% AIBN as initiator (based on acrylic monomers mass) were mixed uniformly and added dropwise into the flask. MPS-SiO₂ as core was coated with a polymer shell to create a core/shell structure, a series of EPAC/SiO₂ were obtained by in-situ solution polymerization at 80°C for 6 h, such as EPAC-1/SiO₂, EPAC-2/SiO₂, EPAC-3/SiO₂, EPAC-4/SiO₂ (containing 0 wt%, 1 wt%, 3 wt%, and 5 wt% M3 as core, respectively), and EPAC-5/SiO₂ (containing 3 wt% M4 as core).

Preparation of EPUAs/SiO₂ composites

The as-prepared EPAC/SiO₂ and N3390 were mixed uniformly, the isocyanate-to-hydroxyl (NCO/OH) and the epoxy group to anhydride molar ratio were preferably about 1.2 and 1, respectively. EPUAs/SiO₂ composites were obtained after cured at 80°C for 1 h and 110°C for 2 h. EPUA-1/SiO₂, EPUA-2/SiO₂, EPUA-3/SiO₂, and EPUA-4/SiO₂ correspond with EPAC-1/SiO₂, EPAC-2/SiO₂, EPAC-3/SiO₂, and EPAC-4/SiO₂, respectively. The synthesis route for EPUAs/SiO₂ is shown in Fig. 1. A network structure of EPUAs/SiO₂ composites is formed by mutually cross-linking functional groups. EPUAs/SiO₂ composites composed of hard and soft segment domain in the polymer matrix, SiO₂ as filler particles were evenly

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