



Synthesis of aqueous highly branched silica sol as underlying crosslinker for corrosion protection



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ABSTRACT

The aqueous hybrid silica sol was prepared by GPTMS and TEOS through sol-gel process. The GPTMS as water-based modifier improved the stability of the aqueous silica sol. The highly branched structure of the aqueous sol was confirmed by Raman spectra and GPC. Using a sol-gel process these aqueous silica sols were incorporated into waterborne polyurethane (WPU). ^{29}Si NMR spectra detected a high crosslinked polysiloxane in composites and connection between silica sol and silanes endcapping WPU (PUS). Dynamic mechanical properties, water absorption, transparency of the composite films have been studied. Scanning electron microscopy (SEM) showed the distribution state of polysiloxane network in composites. It was found that the distribution state of polysiloxane could be greatly influenced by the chemical interaction between PUS and silica sol. The composites had been applied in anti-corrosion coatings. Salt spray test indicated that corrosion resistance of composites had been related to the amount of Si–OH groups.

1. Introduction

Sol-gel science has become an interesting area in research, development and up-coming industrial application during the last 50 years. The versatility of sol-gel chemistry in polymers can introduce newer properties such as reinforce [1], luminescence [2] and optical properties [3] into the resulting material.

In general, sol-gel reaction of siloxane has to take place in organic solvents in order to control the hydrolysis and condensation reaction. It leads to drawbacks in applications, since the volatile organic solvent has to be controlled in coating applications for friendly environment. Under such circumstance, an aqueous silica sol has been developed as the greener alternatives. However, the siloxane exhibits a very high reactivity towards water, making polycondensation reaction in water almost impossible to control [4,5]. To overcome this problem, the nanoparticles or boehmite in particular are introduced into the sol-gel hybrid materials [6,7]. The colloidal silica or boehmite sols could be easily stabilized in aqueous solutions due to electrostatic repulsions [8]. Another strategy, which utilizes chelating agents to control the reactivity of the siloxane, also shows great flexibility in tailoring the physicochemical properties of organic-inorganic hybrid materials [9,10].

Waterborne polyurethane (WPU) has been widely used in a variety of fields such as adhesives, coatings, sealants and so on. However, some inferior properties of WPU as low mechanical strength, solvent and

chemical resistance restrict to some extent their utility for high performance applications. Therefore, it is important to modify WPU with inorganic moieties in order to improve the mentioned properties. These “new” systems are increasing their use because the synergetic effect can only be observed when good compatibility between phase [11,12].

In recent publications, the organosilane groups were incorporated in the WPU chain. During the water evaporation, these silanized WPU could undergo crosslinking reactions to form a stable siloxane linked network. The cured WPU/siloxane networks exhibited superior properties as coating materials. However, the location of organosilane on the WPU backbone would limit its incorporating contents [13,14]. Furthermore, the siloxane networks in WPU could not be optimized. One solution is the addition of silica sol. Silica sol had rich Si–OH groups, which can condense with silanized WPU, and further cured to WPU/Polysiloxane composite. The composite would have a very good physical barrier because the silica sol had offered crosslinked polysiloxane network. On the other hand, the Si–OH groups of silica sol could react with metal hydroxyls (Me–OH). Subsequently the formation of chemical bonding (Me–O–Si) could improve the adhesive ability of WPU/Polysiloxane composites on the metal surface [15–17]. In view of the above, the silica sol could be used as underlying crosslinker for WPU to promote the corrosion protection for metal.

In this work, the aqueous highly branched silica sol was firstly prepared by sol-gel process. To reduce the gel reaction, the 3-Glycidyloxypropyltrimethoxysilane (GPTMS) as water-based modifier

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was used in hydrolysis and condensation reactions with tetraethylorthosilicate (TEOS). The structure of hybrid sols and gels was explored by the Raman and ^{29}Si NMR spectra. Secondly, the silanized WPU prepolymer was synthesized with 3-amino propyltriethoxysilane (APTES) as end-capping agent. After that, the aqueous hybrid silica sol was added into the silanized WPU prepolymer to obtain WPU/Polysiloxane composite. APTES provided strong interaction between the WPU and silica sol, since it could both react with NCO groups of WPU chains and silanol groups in the silica sol. The structure of polysiloxane network in composites was determined by ^{29}Si NMR spectra. The interaction between WPU and polysiloxane was investigated by the dynamic mechanical thermal analyzer. The corrosion protection of composites was evaluated by salt spray testing.

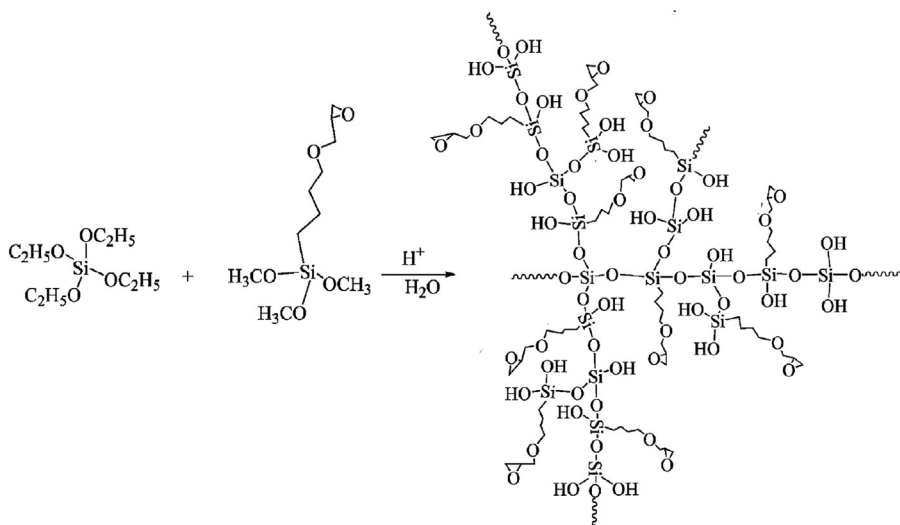
2. Materials and methods

2.1. Materials

Raw materials tetraethylorthosilicate (TEOS), 3-Glycidyloxypropyltrimethoxysilane (GPTMS), 3-Aminopropyltriethoxysilane (APTES) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) was diluted to a concentration of 0.5 mol/L with water. $\text{C}_2\text{H}_5\text{OH}$ and deionized water were used as received. Polypropylene glycol (PPG, M_n 2000 g/mol) was dried at 120 °C under 1–2 mmg H_2 for 2 h before use. 2, 2-Dimethylol propionic acid (DMPA) was dried in a vacuum oven for 2 h at 120 °C. 1, 4-butanediol (BDO) was dried in a vacuum oven for 2 h at 80 °C. Triethylamine (TEA) and acetone were used after dehydration with 4-A molecular sieves for 24 h. Isophorone diisocyanate (IPDI) was purchased from Bayer Chemie A.G.

2.2. Preparation of highly branched silica sols in aqueous medium

The hybrid silica sols were synthesized from GPTMS and TEOS. To ensure a miscible solution of the silane precursors, the ethanol was used as co-solvent in mole ratio of ethanol: siloxane for 1.3:1. The ethanol content in silica sol was below 9 wt%. To improve the stabilization in aqueous medium, a relatively high quantity of HCl (0.5 mol/L) was used as catalyst in mole ratio of HCl: siloxane for 0.1:1. The mixture was stirred at ambient temperature for 24 h. Finally, a clear transparent solution was obtained, and the solid content was 14 wt%. The preparation of the aqueous highly branched silica sol was shown in Scheme 1.



Scheme 1. Preparation of highly branched silica sol.

2.3. Preparation of waterborne polyurethane/polysiloxane composite emulsion

A three-neck glass reactor with a mechanical stirrer and a condenser tube was charged with a proper amount of PPG, DMPA, DBTDL and IPDI. The reaction was conducted in a water bath maintained at 85 °C for 1 h. The BDO was added to the reaction mixture and the reaction was continued until the NCO value reached the theoretical value. The measurement of NCO content was carried out according to the standard titration method (ASTM D 2572-87). After completely reaction, the mixture was cooled to 50 °C and appropriate acetone was added to reduce the viscosity. Subsequently, the reaction temperature was down to 35 °C and TEA was added to neutralize the carboxylic acids of DMPA for 30 min. Then, the mixture of APTES and acetone were charged into the flask and the reaction proceeded at 35 °C for another 2 h. After that, the highly branched silica sol and water were added to the flask under vigorous stirring. Hydrolysis of ethoxy groups in APTES offered silanol groups, which could condense with silanol groups in the silica sol to form siloxane linked network. The sol-gel process of PUS and silica sol was summarized in Scheme 2. Finally, acetone and ethanol were removed under vacuum. The resulting composite emulsion had a solid content of 30 wt%. The recipes to prepare WPU/Polysiloxane composite were shown in Table 1.

2.4. Characterization

The silica sol was extracted by mixture of NaCl saturated solution and THF in mass ratio of 1:1:1. The molecular weight and distribution of silica sol was measured by GPC (PL-GPC120). THF was used as eluent and flow rate was 1 ml/min at 37 °C. The molecular weight was calibrated with polystyrene standards.

Composite films were cast from emulsion on a Teflon plate at ambient temperature for 24 h. The remaining moisture was removed at 80 °C for 4 h.

^{29}Si NMR spectroscopy was used to determine the Si-O-Si cross-linking density of silica gel and composite. Spectra were recorded on a Avance III 500 MHz spectrometer. The power samples or composite films were placed in a rotor sample tube of 4 mm.

The Raman measurements were measured by the Raman spectrometer Holo-Probe 785 (Kaiser Optical), which worked in the range between 3500 and 150 cm^{-1} . The Raman spectrometer was equipped with a 400 mW diode laser with an excitation frequency at 785 nm.

Dynamic mechanical analysis (DMA) was performed with a TA Dynamic Mechanical Thermal Analyzer Q800. The samples were heated

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