



Polyurethane/polyphenylsilsequioxane nanocomposite: From waterborne dispersions to coating films

Qi Li^{a,b,1}, Longhai Guo^{a,b,1}, Teng Qiu^{a,b,*}, Jun Ye^b, Lifan He^b, Xiaoyu Li^{a,b,*}, Xinlin Tuo^{c,**}

^a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China

^b Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China

^c Key Laboratory of Advanced Materials (MOE), Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

Proper building of polymer/polysilsequioxane composite is determined by deep-rooted structural variables. This work focuses on the fabrication of silane-grafted waterborne polyurethane (DWPU)/polyphenylsilsequioxanes (PPSQ) composites by blending and in-situ methods, respectively. By using blending method, PPSQ nanoparticle latexes were dispersed in DWPU. By using in-situ method, as the precursor of PPSQ, phenyltrimethoxysilane was mixed in DWPU, and PPSQ was expected to be generated via in-situ sol-gel reaction during film formation. We systematically investigated the influences of PPSQ and its incorporation method on the phase separation of films. The competition between a heterophase-triggered phase separation and a silane-based crosslinking was found during film formation. The intrinsically local ordering permutation of PU segments was interrupted more or less with PPSQ. Both surface composition and morphology were altered in correspondence to the different addition amount of PPSQ. Furthermore, optical, mechanical, and thermal resistances of composite films were also investigated for potential applications as coatings.

1. Introduction

Polyurethane (PU) is a class of high performance materials composed of rigid diisocyanate-extender blocks (hard segments, HS) linked to a long-chain polyether or polyester macrodiols (soft segments, SS). It has a wide range of applications in various fields, such as CASE (coatings, adhesives, sealants, and elastomers) for furniture, constructions, appliances, automotive seating, footwear, etc. [1]. In the past, PU was mainly synthesized in organic solvents [2]. Recently, with the increasing health and environmental awareness, waterborne polyurethanes (WPU) have been emerged as an important alternative to their solvent-based counterparts. However, WPU are limited in engineering applications by some inferior properties [3,4]. One of the highlighted methods to improve WPU systems is to use inorganic nanocomponents in the overall composition, i.e., to build organic-inorganic (O-I) nanocomposites [5].

O-I nanocomposites have been intensively studied in the field of material science, especially in the last two decades [6,7]. As a new class of materials, O-I nanocomposites combine the excellent properties of both polymer matrix (organic part) and nanofillers (inorganic part). In the development of these materials, organically modified silica or

ormosils and silsesquioxanes (the general formula is $[R_2Si_2O_3]_n$ and R is an organic group or hydrogen) are mostly used [8,9]. The combination of these silica based nanoparticles (SiNP) and WPU has received much attention due to the synergetic effect between SiNP and PU.

SiNP has many advantages, including high hardness, low refractive index, excellent chemical stability, low price, and commercial availability from different sources [10]. Additionally, the synthesis of WPU with enough process flexibility is also feasible for molecular design. Through the choice of organic and inorganic raw materials, tuning their functionalities, relative concentrations and preparation procedures, novel and desired performances are expected. However, the phase separation between the inorganic and the organic phases should be concerned, which has a strong impact on the properties of composite materials. In the special case of WPU, the heterogeneity of the polymer dispersions, both the unique film formation process of particle stacking and the intrinsic phase separation of HS and SS of PU make the condensed structure of polymer films more and more complex. It is essential to study and to control the phase separation in the subtle way both in macro- and micro-size scales, aiming to successfully build O-I materials based on WPU.

According to the literature, a variety of attempts have been made in

* Corresponding authors at: State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China.

** Corresponding author.

E-mail addresses: qiteng@mail.buct.edu.cn (T. Qiu), lixu@mail.buct.edu.cn (X. Li), tuoxl@mail.tsinghua.edu.cn (X. Tuo).

¹ The authors contribute equally to this work.

order to disperse SiNPs in water and/or increase the compatibility between the organic and inorganic phases [11–14]. One basic design is to modify PU by coupling groups like alkoxy silane. And three approaches have been reported on this purpose. The first is to block the PU prepolymers with amino functional silanes, such as aminophenyltrimethoxysilane (APTMS) and aminophenyltriethoxysilane (APTES) [15,16]. It is obvious that the content and the distribution of silane groups would be limited by the molecular weight of prepolymers. The second is to introduce the alkoxy silane groups to polyol through chemical modification reactions [17,18]. However, it is only suitable for the limited cases when special polyol is used, such as castor oil. The third, which we are much concerned, is to graft the silane groups on PU chains as the side groups by using the dihydroxy functionalized alkoxy silane as the chain extender [19,20]. This method is most likely to be adapted to most of the WPU synthesis protocols, on the premise of the proper designed chain extender of silane. For example, in our recent work, we have synthesized a silane diol (DEA-Si) containing trimethoxysilane side groups via Michael addition reaction, and applied it as the chain extender in the synthesis of WPU. The WPU is special because the trimethoxysilane groups are incorporated as the side groups and spaced from the main chain by long alkyl-ester segments. It has been proved that the structure of the long flexible side chain improves the mobility and the availability of the attached alkoxy silanes. We suppose that the DEA-Si modified WPU (DWPU) would have advantages to be applied as the building blocks in the fabrication of O-I composites in waterborne systems.

On the other hand, in the building of composite system of WPU and SiNPs, the inorganic component should be the other important character. It is also noteworthy that polysilsesquioxane (PSQ) provides us another choice besides the commercial silica or ormosil particles. Being an important class of O-I hybrids itself, organic substituents on PSQ ensure the compatibility with the polymer matrix. The different substituents on PSQ also determine their various physical and chemical properties, as well as their omnifarious applications as high performance coatings, insulator layers, lithographic materials, and additives to materials including cosmetics, polypropylene films, and methacrylic resins [21,22]. One of the popularly studied PSQs is the phenyl substituted one, polyphenylsilsesquioxanes (PPSQs), which is concerned owing to their good properties, such as the mechanical performance, thermal resistance, and flame retardancy [23]. The most important, PPSQ nanoparticles can be introduced in our DWPU via two facile ways.

The first way is based on another our previous work on the direct emulsion synthesis of PPSQ particle dispersions [24]. The particles are in the size below 100 nm and stable dispersed in water, which can be easily blended with DWPU to form a composite. The remained alkoxy silane or silanol (the hydrolytic product of alkoxy silane) can condense with the silane or silanol groups attached on PU, so that the incompatibility between the organic and the inorganic phases is possibly depressed.

Another way is based on the principle of in-situ sol-gel reactions. The basic synthesis reaction of PSQ is the hydrolysis and condensation of trialkoxy silane, and the active groups attached to PU are also the same. So it is reasonable to consider if the precursor silane can be directly introduced into DWPU by partially hydrolysis and maybe gently co-condense with the polymer. The product could also be applied as coating films. The water evaporation would drive the chemical balance toward the co-condensation direction, i.e. the in-situ formation of PPSQ in the films. With the participation of the active groups on WPU chains in the condensation, the formation of a much denser crosslinking network is also expected. However, few of the publications have been seen on the preparation of WPU/PSQ composites aiming at film formation applications, nor the detailed study on the influence of different preparation method on the structure especially the phase separation characteristics as well as the properties of the composite films.

Here, we prepared the DWPU/PPSQ nanocomposite films via two different methods in the name of the blending (BL) and in-situ (IS)

methods as described above. The DWPU was first synthesized via pre-polymer method by using DEA-Si as the chain extender. In the BL method, pre-made PPSQ nanoparticles were synthesized and mixed with DWPU in dispersions. In the IS method, as the precursor of PPSQ, phenyltrimethoxysilane (PTMS), was directly added in DWPU dispersion. Hydrolysis and co-condensation of the active trialkoxy silane bonded on different components of DWPU, PPSQ, or PTMS led to the formation of different but stable composite dispersions, which could be applied as the surface coatings to form continuous films. During the film formation process of the IS dispersions, PPSQ phase was formed via in-situ sol-gel process with the incorporation of DWPU, which was quite different from the film formation of the BL dispersions containing pre-made PPSQ particles. So, in the following work, we applied the various characterizations to reveal the influence of different PPSQ amounts, as well as the introduction method, on the phase and surface structure of the coating films. The impact of the structural evolution on the film properties was also discussed in detail in the work.

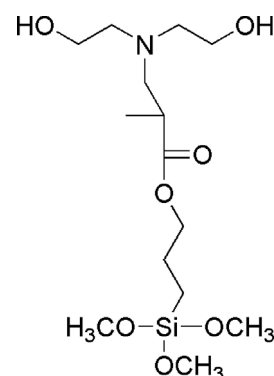
2. Experimental section

2.1. Materials

Isophorone diisocyanate (IPDI) was obtained from Bayer Chemie A.G. 2,2-bis(hydroxymethyl) butyric acid (DMBA) was purchased from Dongyang Tianyu Chemical Co., Ltd. Polycarbonate diol (PCDL, Mn ca. 2000 g/mol) was supplied by Shandong Jining Huakai Resin Co., Ltd. DMBA and the PCDL were dried in a vacuum oven at 80 °C for 24 h before use. Diethanolamine (DEA) was purchased from Tianjin Guangfu Fine Chemical Research Institute. 3-(methacryloxypropyl)trimethoxysilane (MAPTS) was obtained from Nanjing Xiangqian Chemical Co., Ltd. Sodium hydroxide (NaOH) was purchased from Beijing Chemical Works. Polyoxyethylene (10) octylphenyl ether (OP-10) and sodium dodecyl sulfate (SDS) were obtained from Tianjin Fuchen Chemical Reagent Factory. Triethylamine (TEA) was purchased from Tianjin Fuchen Chemical Reagent Factory. Dibutyltin dilaurate (DBTDL) catalyst was obtained from Tianjin Guangfu Fine Chemical Research Institute. 1,4-butanediol (BDO) was purchased from Beijing Chemical Works. Phenyltrimethoxysilane (PTMS) was obtained from Shandong Qufu Chenguang Chemical Co., Ltd. Acetone was purchased from Beijing Chemical Works and was dried over 4 Å molecular sieves at least one week before use. The self-made deionized water was used in the experiment.

2.2. Preparation of DWPU dispersions [25]

The introduction of alkoxy silane side-groups into WPU is based on the self-synthesized alkoxy silane diol (DEA-Si), whose structure is shown in Scheme 1. In the synthesis of DEA-Si, DEA (8.4 g, 0.08 mol) was introduced into a 100 mL of three-neck flask equipped with a mechanical stirrer, a nitrogen inlet and out-let. MAPTS (19.84 g,



Scheme 1. Chemical structure of DEA-Si.

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