



Abrasion resistance of waterborne polyurethane films incorporated with PU/silica hybrids



Wuhou Fan^{a,b,c}, Weining Du^a, Zhengjun Li^{a,*}, Nianhua Dan^a, Jin Huang^a

^a National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

^b Sichuan Textile Scientific Research Institute, Chengdu 610072, China

^c High-tech Organic Fibers Key Laboratory of Sichuan Province, Chengdu 610072, China

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ABSTRACT

We describe polyurethane (PU)/silica hybrids (PSHs) prepared through hydrolysis and condensation reactions of tetraethoxysilane (TEOS) with or without methyltriethoxysilane (MTES) in the presence of polyurethane dispersion, which were subsequently incorporated into waterborne polyurethane (WPU) to prepare composites. The effects of the solid mass ratio of PSHs/WPU on the particle size of composite emulsions, the dispersion of silica nanoparticles in composite films, and the hardness and abrasion resistance of the corresponding films were examined. Composite emulsions possess a nanoscale particle size when incorporated with PSHs prepared using TEOS and MTES as precursors, and are superior to those with PSHs prepared using TEOS alone. Transmission electron microscopy revealed that silica nanoparticles had a uniform distribution in the polymer matrix and agglomerates could be almost completely avoided through *in situ* modification of silica with Si-CH₃ groups in the polyurethane dispersion. Composite films prepared with this method exhibited a superior hardness and abrasion resistance even at a lower silica content compared with that containing unmodified silica. In particular, optical microscopy and scanning probe microscopy observations demonstrated wear behavior differences among these composite films from the macro- and nanoscale viewpoints, respectively. It is proved that abrasive wear occurs, and surface morphology studies are in accordance with the results of abrasion resistance tests.

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1. Introduction

Polyurethanes are an important and versatile class of polymeric materials which can be efficiently prepared to give tailor-made properties by reaction with a great variety of commercially available monomeric materials. They have therefore been widely used as coatings and adhesives to meet diverse performance requirements in many fields such as the automotive, construction, textile, paper, and leather industries for several decades [1–5]. With increasing regulatory pressure and awareness of the need for health and environmental protection, waterborne polyurethane (WPU), as an important alternative to its solvent-borne counterpart, has received much attention due to its zero/low volatile organic compounds emissions, especially when it is used as a coating material [6]. However, mechanical properties (e.g. stiffness, surface hardness), thermal stability and abrasion resistance of WPU films are inferior to those of solvent-borne polyurethane cross-linked films

since WPU usually belongs to one component and thermoplastic systems with a low pre-crosslinked density in order to achieve a good dispersion stability [3,7,8]. These issues greatly limit further application of WPU.

Abrasion resistance, which prevents substrates from being worn by friction, is one of the essential properties of coating materials [9]. It is therefore necessary to enhance the abrasion resistance of WPU to meet the continuously increasing performance requirements for application in coatings. Because the majority of polymeric materials including polyurethanes do not possess sufficient abrasion resistance, their esthetic appearance and durability are vulnerable to damage under constant use [10]. Several attempts have been made to improve the abrasion resistance of polyurethanes. A generally accepted method is the incorporation of inorganic nanoparticles into a polymer matrix [11–18]. Among these inorganic nanoparticles, silica nanoparticles are the most efficiently used and extensively studied due to their commercial availability and low cost. For instance, the surface hardness and abrasion resistance of polyurethane coatings showed an optimal level of enhancement with a silica content of 3.0 wt% [13], and their abrasion resistance could be further improved by the

* Corresponding author. Tel.: +86 28 85408868.

E-mail address: lizhengjun@scu.edu.cn (Z. Li).

addition of silane coupling agents (SCAs) [1,14]. In most cases, uniform dispersion of silica nanoparticles within the polyurethane matrix at the nanoscale level as well as good compatibility and strong interfacial interaction between the silica and the polymer matrix play important roles in improving the abrasion resistance of polyurethanes [19,20]. However, up to now, almost all studies focused on the surface hardness and abrasion resistance of solvent-borne polyurethane composite coatings on rigid substrates. Fewer studies have been carried out on WPU composite coatings on substrates, especially flexible fabric, leather and paper. This has limited application of WPU as an anti-abrasion coating.

Although nanoparticles have been widely employed to prepare polymer composite materials with advanced properties due to the synergistic advantage of nanoscale dimensions, they tend to form agglomerates after incorporation into the polymeric matrix, leading to segregation of the inorganic particles or limited improvement of the properties of the composite materials [21]. Generally, SCAs are used to modify nanoparticles since their active groups can react with the hydroxyl groups of nanoparticles. The attachment of SCAs to nanoparticles can prevent aggregation to some extent due to the steric repulsion of the grafted silane molecules. However, aggregation may still occur because of the inability of modified nanoparticles to re-disperse in an aqueous system due to their hydrophobicity, and their insufficient compatibility with the polymer matrix due to the low surface energy of the grafted silane molecules. To avoid problems of agglomeration during re-dispersion, a simple and convenient route was recently proposed to modify nanoparticles *in situ* using polymers which function as diluting and de-agglomerating agents. The modified nanoparticles were then incorporated into an organic host matrix to prepare composites [22–24]. Because the surface properties of nanoparticles were changed from hydrophilic to lipophilic, both the uniform dispersion of nanoparticles in the host matrix and better compatibility between the inorganic and organic moieties were achieved. This is beneficial for decreasing or even avoiding agglomeration in the host polymer matrix, and composites with improved abrasion resistance could be obtained. In fact, this method was shown to improve the abrasion resistance of a polymer with silica content lower than 2.0 wt% [22].

In the present study, PU/silica hybrids (PSHs) with pre-dispersed silica nanoparticles were prepared *in situ* through hydrolysis and condensation reactions of tetraethoxysilane (TEOS) with or without methyltriethoxysilane (MTES) in the presence of polyurethane dispersion without addition of an external catalyst. The PSHs were further incorporated into WPU emulsions to prepare composite emulsions, and then the corresponding composite films were obtained in order to evaluate their abrasion resistance. The particle size and distribution of the PSHs and composite emulsions were characterized using a particle size analyzer. The dispersion of silica nanoparticles in the composite films was viewed using transmission electron microscopy (TEM). Shore A hardness and wear mass loss of the composite films were tested by a Shore A hardness tester and Taber abraser, respectively. The surface morphology of the composite films at the macro- and nanoscale levels were also observed using optical microscopy (OM) and scanning probe microscopy (SPM), respectively, the object being to reveal wear mechanisms that may exist during the abrasion resistance test.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, Analytical grade) and methyltriethoxysilane (MTES, Analytical grade), supplied by Chengdu Kelong

Table 1
Basic parameters of the polyurethane dispersion and WPU emulsion.

Ingredients	Solid content/%	pH value	Average particle size/nm	PDI
Polyurethane dispersion	22.8	8.0	70.84	0.109
WPU emulsion	20.0	8.0	94.99	0.098

Chemical Reagent Factory (Chengdu, China) and Xiantao Blue Sky Chemical Co., Ltd. (Xiaotao, China), respectively, were used without further purification. Commercially available polyurethane dispersion (Melio Promul 56.B) and WPU emulsion (PU3033) were obtained from Clariant (Muttenz, Switzerland) and Shengfang (Jiangmen, China), respectively.

2.2. Synthesis of PSHs

TEOS was employed as an inorganic precursor for the preparation of silica and MTES was used for surface modification of the generated silica. The polyurethane dispersion was employed as a diluting and de-agglomerating agent of the silica nanoparticles in the preparation of PSHs. Basic parameters of the polyurethane dispersion are shown in Table 1. Two types of PSH, namely PSH-A and PSH-B, were prepared through sol-gel reactions of TEOS with or without MTES in the presence of polyurethane dispersion, according to the method reported by Yeh et al. [25]. PSH-A and PSH-B refer to PSHs prepared with TEOS and mixtures of TEOS and MTES as the inorganic precursors, respectively.

A 250-mL round-bottom, three-necked flask with a mechanical stirrer and thermometer was used as a reactor, and reactions were carried out in a constant temperature water bath. The polyurethane dispersion and inorganic precursors were first blended by stirring

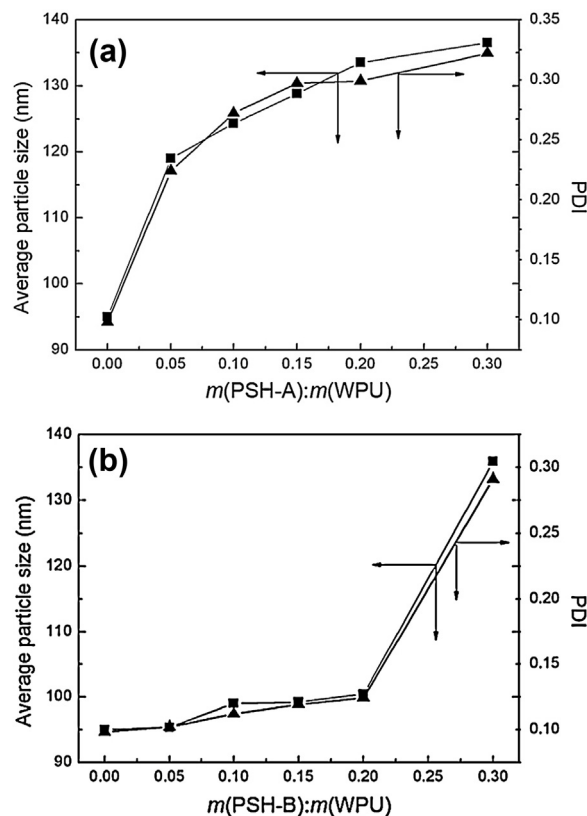


Fig. 1. Average particle size and PDI of the composite emulsions as a function of $m(\text{PSH-A}):m(\text{WPU})$ (a) and $m(\text{PSH-B}):m(\text{WPU})$ (b) (the mean values of three emulsion samples).

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