

# Effect of flexibility of grafted polymer on the morphology and property of nanosilica/PVC composites

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## Abstract

In this study, poly(methyl methacrylate)-grafted-nanosilica (PMMA-g-silica) and a copolymer of styrene (St), *n*-butyl acrylate (BA) and acrylic acid (AA)-grafted-nanosilica (PSBA-g-silica) hybrid nanoparticles were prepared by using a heterophase polymerization technique in an aqueous system. The grafted polymers made up approximately 50 wt.% of the resulted hybrid nanoparticles which showed a spherical and well-dispersed morphology. The silica hybrid nanoparticles were subsequently used as fillers in a poly(vinyl chloride) (PVC) matrix to fabricate PVC nanocomposite. Morphology study of PVC nanocomposites revealed that both PMMA- and PSBA-grafted-silica had an adhesive interface between the silica and PVC. The tensile strength and elongation to break were found to be improved significantly in comparison with that of untreated nanosilica/PVC composites. Finally our results clearly demonstrated that the properties (e.g. chain flexibility, composition) of the grafted polymer in the hybrid nanoparticles could significantly affect the dispersion behavior of hybrid nanoparticles in PVC matrix, dynamic mechanical thermal properties and mechanical properties of the resulted PVC composites.

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## 1. Introduction

In polymer-nanoscale filler composites research, the primary goal is to enhance the strength and toughness of polymeric components using molecular or nanoscale reinforcements [1]. In addition to various layered silicates such as montmorillonite [2] and spherical mineral particles such as calcium carbonate [3–5] and aluminum oxide [6], silica has played an important role in reinforcement components due to nanoscale effects [7], polymer–silica nanocomposites often exhibit dramatic improvements in strength, modulus, heat resistance, and gas permeability barrier properties.

Nanosilica, because of a large surface area, is easy to generate silica aggregates embedded in a polymer matrix and resulting in none of the anticipative enhancement in mechanical properties [8]. Therefore, the surface modification of nanoscale fillers becomes necessary in the preparation of nanocomposites.

Nanoscale fillers are usually organically modified in order to reduce the filler aggregation and enhance the interaction between the filler and polymer matrix, consequently acquiring a uniform dispersion of the filler in the polymer matrix.

Nowadays grafting polymers onto silica surfaces is attracting more and more interest due to their important applications ranging from colloidal stabilizers [9,10] to nanocomposite materials [11,12]. Currently the technologies for filler surface treatment include atom transfer radical polymerization (ATRP), sol–gel processing, *in situ* intercalative polymerization, *in situ* polymerization and so on [13,14]. The resulting polymer shell covered on the nanosilica can improve the dispersion of fillers into polymer matrix and produce extra interactions between polymeric shell and matrix.

Polyvinyl chloride (PVC) materials have extensive applications, such as pipes, electric cables and sectional bars, etc. Within recent years, great attention has been paid to modify and toughen PVC. Rubber is widely used to toughen PVC composites. However, it often leads to a reduction in strength, heat resistance, modulus and difficult processing of the polymeric composites [15–17]. Rigid inorganic nanoparticles,

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such as calcium carbonate, silica, can improve the tensile strength, electric properties, and heat resistance of the PVC composites [18–20]. However, the interfacial interaction between the inorganic nanoparticles and PVC matrix still cannot be solved. Pukanszky [21] proposed that the dimension of interface and strength of the interaction significantly influence the ultimate tensile properties of the composites. Jancar and Kucera [22,23] believed that poor adhesion between polypropylene (PP) and  $\text{CaCO}_3$  resulted in a decrease in the tensile yield stress with increasing volume fraction of  $\text{CaCO}_3$ . However, it is found that the tensile properties of  $\text{CaCO}_3$ /PP composites increased by introducing PP-grafted-maleic anhydride (PP-g-MAH), which enhanced the interfacial interaction between the PP matrix and  $\text{CaCO}_3$  particles. To improve the adhesion between the matrix and inorganic particles, a coupling agent and polymer were employed to modify the surface of inorganic particles. Wu et al. [24] blended PVC with nano- $\text{CaCO}_3$  particles coated with a chlorinated polyethylene (CPE) elastomer and found that the composites had higher tensile and impact strength than those blended with untreated particles. Though treatment of nanoparticles through graft polymerization and application of grafting nanoparticles in making polymer composites have been investigated widely, the effect of flexibility of grafted polymer on the interfacial morphology and property of nanosilica/PVC composites has not been reported.

In this study, hybrid nanoparticles with different flexibility of grafted polymer were firstly prepared by using a heterophase polymerization technique in an aqueous system. The treated nanosilica was subsequently used to fill PVC. It was expected that the polymer covered on the nanosilica could improve the mechanical properties of the resulting PVC nanocomposites. Moreover, the interfacial properties of the composites can be tailored by varying the flexibility of the grafted polymer, which leads to a strong but flexible interface consequently.

## 2. Experimental

### 2.1. Materials and sample preparation

Fumed silica ( $\text{SiO}_2$ ) nanoparticles were supplied by Shanghai Chemical Co., China with an average diameter of 25 nm. The particles were dried at 120 °C under vacuum for 24 h to eliminate the physically absorbed and weakly chemically absorbed species. Silane coupling agent ( $\gamma$ -methacryloxypropyl trimethoxy silane (MPS)) was provided by Nanjing Shuguang Chemical Industry Co. Ltd., China. Technical-grade monomers methyl methacrylate (MMA), *n*-butyl acrylate (BA), styrene (St), both with 10–20 ppm of hydroquinone monomethyl ether (MEHQ), acrylic acid (AA) purity of 99% were purchased from by Guangzhou Langri Chemical Co., Ltd., China. The monomers were purified before use. The emulsifier nonyl phenol polyoxyethylene ether (OP-10), sodium dodecyl sulfate (SDS) and kalium persulfate (KPS) were used as supplied. Doubly deionized water (DDI water) was used throughout the work. Suspension PVC (WS-800, DP = 800) was produced by Shanghai Chlor-Alkali Chemical Co., Ltd., China. The organic tin stabilizer and stearic acid were industry grade products.

### 2.2. Introduction of double bonds onto nanosilica

Pre-treatment of silica nanoparticles with a silane coupling agent was carried out as follows, to introduce double bonds onto nanosilica. An excess of the coupling agent was added to a suspension of nanosilica in toluene solution. After ultrasonic agitation for 30 min, the suspension was refluxed for 10 h under the protection of dry nitrogen flow. Afterwards, the nanosilica was filtrated and extracted with ethanol for 24 h to remove the excess silane absorbed on the particles, and then the silane treated nanosilica was dried in vacuum at 50 °C for 24 h.

### 2.3. Preparation of polymer-grafted-silica hybrid nanoparticles

The polymerizations in the presence of functionalized nanosilica were performed by the following process: 1 g of the functionalized nanosilica was dispersed in the aqueous solution, in which 2 g of isopropanol, 0.03 g SDS and 0.015 g of OP-10 and 95 ml of DDI water were added. Having experienced ultrasonic agitation for 30 min, the suspension was poured into the a 250-ml jacketed glass reactor equipped with reflux condenser, thermocouple, stainless-steel stirrer, nitrogen inlet and heated under constant stirring (130 rpm) with protection of nitrogen flow. Once the reaction temperature was reached (75 °C), the aqueous solution of initiator (0.01 g of KPS solution) was added slowly drop by drop. After 10 min, a continuous dosage of the monomer was added under monomer-starved conditions. After 3 h, when initiator and monomer have been added into the reactor, another 0.5 h reaction at 80 °C was required to improve the monomer conversion. The obtained products were dried at 45 °C under vacuum after emulsion centrifugation and washing process. The polymerization products were extracted with acetone for 24 h in a Soxhlet apparatus to remove the un-grafted polymer and dried to a constant weight under vacuum.

With the above heterophase polymerization technique, PMMA-g-silica and PSBA (48 wt.% styrene, 48 wt.% *n*-butyl acrylate and 2 wt.% acrylic acid (AA))-g-silica hybrid nanoparticles were obtained respectively.

### 2.4. Preparation of hybrid nanoparticle filled PVC composites

The PVC matrix used in this investigation has the following composition: 100 parts PVC, four parts heat stabilizer (organic tin), two parts process aid (ACR401), 0.6 parts oxidized polyethylene (OPE) and 0.5 parts stearic acid. Hybrid nanoparticles and untreated nanosilicas were mixed with the PVC matrix mixture in a high-speed mixer. The silica weight fraction was kept at 2.5 wt.% for all the composites. The PVC compound and nanoparticles were plasticized by a two-roll mixer at 180 °C for 10 min. Composite plates with dimensions of 200 mm × 80 mm × 3.2 mm were compressed molded at 180 °C for 8 min, with a 5-min preheating period. Care was taken at this stage to ensure precise timing so as to eliminate any differences that might arise as a result of the samples

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