



Fabrication of retro-reflective polyurethane via covalently embedding with amino-functionalized glass microspheres

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ABSTRACT

Amino-functionalized glass microspheres (NH₂-GM) grafted with 3-aminopropyltriethoxysilane (APTS) were synthesized and well characterized by X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and scanning electron microscope (SEM). Then the NH₂-GM was covalently incorporated into polyurethane (PU) matrix through urea linkages to fabricate a composite with retro-reflective effect, and the influence of NH₂-GM content on the retro-reflective performance, glass transition temperature, morphology structure and mechanical properties of the resultant glass microspheres based retro-reflective polyurethane (GMPU) were investigated. Results demonstrate that GMPU maintains initial retro-reflective properties and reflects bright light under vertical angle incidence in darkness. Moreover, compared with PU directly blending with GMs (GM/PU), GMPU shows clear improved compatibility and interfacial interactions between PU and NH₂-GMs, as evidenced by the higher glass transition temperature and enhanced mechanical properties of GMPU hybrids.

1. Introduction

Glass microspheres (GMs) are one of the commonly used inorganic retro-reflective materials, which can reflect light back in a very narrow beam along approximately the same angle from the incident direction [1,2]. Different from the planar mirror, the entrance angle at which GMs reflect light by this means is greater than zero. Based on this unique property, GMs have been extensively applied to road signage [3–5], building [2], safety clothing and textile and leather [6,7], so as to provide higher night visibility.

In the past few years, directly blending GMs with the polymer has demonstrated to be an efficient method to prepare retro-reflective composites [8,9]. However, due to the nature of smooth spherical surface, the interfacial adhesion between GMs and the polymer matrix is believed to be relatively weak [10], resulting in the voids of the substances over short-term use, which is undesirable in many applications [8]. In addition, physical particle-filled polymer/GM composites usually exhibit deteriorated mechanical properties on account of the fundamentally different structures between the rigid inorganic particles and organic polymers [11]. Given this situation, a feasible route to overcome the poor compatibility and interfacial interactions between GMs and polymer matrixes would be conjugating the GMs into polymer chains via covalent linkages. To provide active sites, the GMs are

necessary to be functionalized before incorporation into appropriate polymer matrixes. Kisang Ahn et al. [12] functionalized glass microspheres by sulfonated polyphenylene oxide, and then they were introduced into the sulfonated polyphenylene oxide matrix, endowing the final matrix desired mechanical properties because of the improved interfacial adhesion between the sulfonated polyphenylene oxide and the functionalized glass microspheres. B.L. Zhu and coworkers [13] reported a GMs filled LDPE-matrix, which was filled by suitable amount of silane coupling agent modified GM, exhibits higher thermal conductivity.

Considering that the polymer/GMs composites are often used in hostile environment weather, the selected polymeric resins are supposed to have advantages of both high and low-temperature tolerance, sunlight ageing resistance, anti-moisture as well as long weatherability, such as polyacrylic acid, epoxy resin and polyurethane. Among them, polyurethane (PU) is a promising material, which has been applied in a very wide range of commercial and industrial fields including road signage, building coating, textiles and leather finishing, due to its numerous benefits, such as good hydrolysis resistance, broad workable temperature range, excellent resistance to yellowing of aliphatic one [14–20]. Particularly, with the enhancement of people's environmental awareness, traditional solvent-based polyurethanes are gradually replaced by waterborne polyurethanes (WPU) [21–23] and solvent-free

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polyurethanes [24,25]. However, as far as we know, comparatively little work has been performed on the chemically combination of glass microspheres with solvent-free polyurethanes up to date.

In this study, we demonstrate the fabrication of amino-functionalized GMs (NH₂-GM) by decorating 3-aminopropyltriethoxysilane (APTS) on the surface of hydroxylated glass microspheres based on the structural feature of polyurethane [26], which serve as anchoring sites to prepare GMs-based retro-reflective polyurethane (GMPU) through irreversible chemical method “bridge” by urea linkages. It is anticipated that the covalent conjugation could effectively improve the compatibility and interfacial interactions between PU matrix and GMs solids, and endow GMPU with favorable retro-reflective effect.

2. Experiment

2.1. Materials

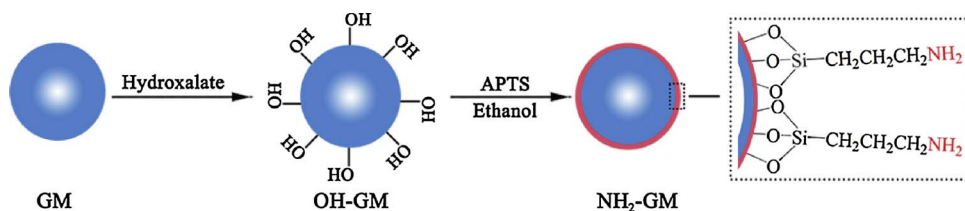
NaOH, 3-Aminopropyltriethoxysilane (APTS) and n-propylamine were purchased from Kelong Chemical Co. Ltd. (Chengdu, China). Glass microspheres were supplied by Weicaixiang Technology Ltd. (Shenzhen, China). Isophorone Diisocyanate (IPDI), 1,6-Diisocyanatohexane (H₁₂MDI), N-Methyl monoethanolamine (MMEA) and 1,4-Butanediol (1,4-BDO) which was dried at 120 °C under high vacuum (0.8 mmHg) overnight before use were bought from Aladdin Industrial Corporation (Shanghai, China). Poly(propylene glycol) with a molecular weight of 2000 (PPG220) and 1000 (PPG210) was purchased from Xiya Reagent Co., Ltd (Chengdu, China) and dried at 120 °C under high vacuum (0.5 mmHg) for 12 h before use. Bismuth neodecanoate was provided by Deyin Chemical Co. Ltd. (Shanghai, China). All chemicals were of analytical grade and used as received without further purification.

2.2. Fabrication of amino-functionalized GM

To synthesize hydroxy-functionalized GM (OH-GM) firstly, 10 g GM and 200 mL NaOH solution (0.5 mol/L) were added to the flask with the aid of ultrasound to form a homogeneous solution, followed by stirring at 90 °C for 1 h to attach hydroxyl groups on the surface of GM. After cooling down to room temperature, the solid was filtrated and washed several times by deionized water, and dried at 80 °C under vacuum. 8 g of the as-synthesized OH-GM was re-dispersed in 160 mL ethanol under ultrasonication, and excess amount of 3-aminopropyltriethoxy silane (APTS, 20 wt.%) and n-propylamine (0.2 g) as catalyst were charged into the aforesaid dispersion under vigorous stirring at 60 °C for 1 h in N₂ atmosphere to fabricate amino-functionalized GM (NH₂-GM). The final NH₂-GM was collected after filtration, washed with ethanol and dried in vacuum at 80 °C for 24 h. The reaction route to NH₂-GM is depicted in Scheme 1.

2.3. Synthesis of prepolymer

IPDI, PPG 220, PPG 210 and 1, 4-BDO (molar ratio of IPDI: PPG 220: PPG 210: 1, 4-BDO = 9: 2: 1: 2, molar ratio of NCO: OH = 1.8: 1) were mixed and poured into the four-necked flask equipped with a thermometer, mechanical stirrer, nitrogen inlet and condenser with a drying tube. Then calculated amount of bismuth neodecanoate (0.05 wt %) was added to the mixture and reacted with atmosphere of nitrogen



Scheme 1. Schematic representation for synthetic route to NH₂-GM.

agitation at (80 ± 2) °C for 2 h. When the residual isocyanate ester content approached to the theoretical value, the temperature of the system was cooled down to 50 °C. Successively, the hydroxyl-terminated polyurethane prepolymer was obtained after blocked by MMEA (molar ratio of IPDI: MMEA = 9: 8) for another 0.5 h.

2.4. Preparation of GM-based retro-reflective polyurethane (GMPU)

Appropriate quantities of prepolymer and H₁₂MDI (molar ratio of NCO: OH = 1.2: 1) were mixed uniformly with the presence of bismuth neodecanoate, and were transferred onto the polytetrafluoroethylene plate. Then the NH₂-GMs (10 wt%) were sprinkled on the surface and pressed with a pressure that would partially-embed the microspheres into the polyurethane mixtures. After that, the resulting composites were put into an oven and cured at 100 °C for 1 h to form glass microspheres-embedded retro-reflective polyurethane (GMPU). The curing process is presented in Scheme 2. For comparison, the blend sample was also prepared in a similar procedure except that the NH₂-GM was replaced by equal quality of unmodified GM, and the resultant composite was abbreviated as GM/PU. It is worth noting that the small amount of -NH₂ in NH₂-GM hardly influences the ratio of final polyurethane, and the amount of the other materials remains unchanged.

2.5. Characterization

The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, ThermoFisher Scientific, USA). Thermogravimetric analysis (TGA) was carried out with TG-209F1 thermal analyzer (NETZSCH, Germany) under nitrogen atmosphere at a constant heating rate of 10 °C/min. The morphology of glass microspheres and polyurethane were observed by a scanning electron microscope (JSM-6360LA, JEOL Ltd., Japan). FT-IR spectra were performed by a Nicolet IS10 FTIR spectrometer (ThermoFisher Scientific, USA) from 400 to 4000 cm⁻¹ after 32 scans with a resolution of 2 cm⁻¹. The curing kinetics of PU and GMPU were measured on a differential scanning calorimeter (DSC200 PC, NETZSCH, Germany) with a thermal analysis data station, operating at a heating rates of 5, 10 and 20 K/min under nitrogen atmosphere. The RoadVista 932 handheld retroreflectometer (RoadVista, USA) was used to measure the retro-reflective performance with the observation angles at 0.2° and entrance angles of 0, ± 5, ± 15, ± 30 and ± 45, respectively. Dynamic mechanical analysis was conducted using a Dynamic Mechanical Analyzer (DMAQ242C, NETZSCH, Germany) under a nitrogen atmosphere at a frequency of 1 Hz and a heating rate of 3 °C min⁻¹ over a temperature range of -80 to -10 °C. The tensile properties were carried out at room temperature using a universal material testing machine (model tensiTECH) supplied by Tech-Pro Inc. (Woodstock, USA). The samples were cut into 50mm × 10 mm dumb-bell shape with thickness of around 0.5 mm and the crosshead speed was set at 100 mm/min according to ASTM D 638 in room temperature. Each sample was measured five times and the average values as well as their standard deviation were reported.

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