



Tuning the interface between poly(vinylidene fluoride)/UV-curable polysilsesquioxane hybrid composites: Compatibility, thermal, mechanical, electrical, and surface properties



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ABSTRACT

Compatible hybrid composites (PVLPMMA) comprising of poly(vinylidene fluoride) (PVDF) and UV-curable ladder-like polysilsesquioxane (LPMASQ) were investigated for maximizing synergetic effects in various properties. The PVDF fluoropolymer was found to be well-incorporated with the LPMASQ inorganic filler because of good hydrogen-bonding, and the compatibility rigorously investigated by FT-IR, DSC, and WAXS studies. In addition, the crosslinkable function arising from the methacryl-group of the LPMASQ inorganic filler with the aid of the radical source was evaluated from the analysis of various properties. After UV-crosslinking, PVLPMMA hybrid composites showcased enhanced mechanical properties such as elastic modulus, surface modulus, and surface hardness with accordance to the increasing the LPMASQ quantity. In addition, hydrophobicity was observed through the increase in the water contact angle up to 115°, a value much larger than that of neat PVDF and cured LPMASQ. Furthermore, the enhanced electrical stability of PVLPMMA hybrid composites was obtained through examination of dielectric properties and breakdown strength in comparison to neat PVDF. These PVDF-LPMASQ organic-inorganic compatible hybrid composites with enhanced properties arising from the good compatibility and synergetic effects can be applicable in the various fields supplanting neat PVDF.

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1. Introduction

Over the past several decades, the demand for new and enhanced properties have led scientists to endeavor polymer nanocomposites to mitigate the drawbacks of singular component systems, while bolstering the advantages of both components due to synergetic effects [1–3]. By simply blending two different components, the enhancement of a myriad of properties have been reported for a wide range of potential applications [4,5]. The widespread use of polymers only reinforces the utility of the blend methodology, as polymer blending is believed to one of most

efficient and simple ways to prepare highly enhanced performance materials.

One of the most extensively researched group of polymers are fluorinated polymers involving poly(vinylidene fluoride) (PVDF) and its copolymers. Due to the polar dipoles induced by the fluorine groups on the main chain backbone, these crystalline polymers are known to have a wide range of favorable traits including good processibility, high chemical resistance, high dielectric constant, good mechanical, and ferroelectric properties [6,7]. Although, the aforementioned properties make fluorinated polymers of the most promising materials, these polymers have shown lack of electrical, mechanical, and surface properties for use in such applications of electrical insulators, protecting films for electrical devices, and mechanically stable membranes because of their typical nature [8,9]. To this end, polymer composites incorporating highly reinforcing inorganic fillers have been substantially demanded to

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effectively enhance aforementioned properties. Investigations into their thermal, mechanical, electrical, morphological, and surface properties have revealed the optimization of the above properties through a versatile blend methodology. Although numerous studies have detailed PVDF-based polymers blended with inorganic fillers, these hybrid composites have still suffered from inhomogeneous defects arising from compatibility issues from inorganic-organic biphasic composites [10,11].

Compatibility in organic-inorganic hybrid composites is one of the most important parameters dictating their composited properties [12]. Meanwhile, incompatible polymer blends usually exhibit complex multiphase morphologies formed during sample preparation, which undeniably affects their mechanical, electrical, and morphological properties of the final composites. Compatibility between organic polymers usually depends on a variety of factors including melting behavior, chemical or physical interactions between polymer chains, and solubility [13]. Various studies of PVDF-based polymer nanocomposites have been investigated, notably with poly(methyl methacrylate) (PMMA) and functionalized inorganic reinforcing materials with PMMA [14–16]. These studies have focused on physical interaction of the hydrogen groups in PVDF with the polar carbonyl functionalities of methacrylate. Due to their good compatibility, significantly enhanced properties of hybrid composites have been extensively reported [17,18].

Polysilsesquioxanes are inorganic-organic hybrid materials with chemical formula $[\text{RSiO}_{1.5}]_n$ [19]. The internal structure of the inorganic Si–O–Si network formed by hydrolysis-polycondensation dictates the overall structure of the network as either random, cage (also known as POSS), or ladder-like [19–24]. Due the inorganic and organic phases being covalently bonded to one another, the limitations with inhomogeneities arising in conventional organic-inorganic hybrid composites can be neglected, leading to highly compatible polymer composites with other organic polymers. A literature search revealed that only a few reports have investigated the preparation of hybrid POSS-PVDF composites, most likely due to the inability of conventional polysilsesquioxane materials to form mechanically robust free-standing films [25–27]. Moreover, the structural defects of random-structured polysilsesquioxanes containing significant amounts of uncondensed Si–OH groups does not allow for good solubility, or high molecular weight.

Ladder-like polysilsesquioxanes (LPSQs) are a unique structural subclass of polysilsesquioxanes in which the Si–O–Si bonds comprise a double-stranded ladder-like structure [22–24,28,29]. Due to the structural regularity and highly condensed nature of the internal double-stranded bonds, LPSQs can be synthesized with high molecular weight, leading to superior mechanical, thermal, low dielectric, hydrophobic properties, and exceptional compatibility with polymer matrixes owing to the function of organic component while maintaining high solubility in a wide range of solvents. In this study, we utilized a LPSQ containing both phenyl and methacryl groups (LPMASQ) [23] and prepared PVDF-LPMASQ hybrid compatible composites through a simple solution blend process. These hybrid composites were designed to achieve the maximized synergetic effects in thermal, mechanical, electrical, morphological, and surface properties owing to the highly compatible nature of PVDF and LPMASQ. For this, the methacryl functional groups in LPMASQ served dual functions: (1) to induce good compatibility of LPSQ into the PVDF matrix, and (2) UV-curing under mild conditions to give randomly multi-networked hybrid composites, resulting in substantially enhanced thermal, mechanical, electrical, and hydrophobic properties. To the best of our knowledge, this is the first report evaluating the compatibility of PVDF-polysilsesquioxane hybrid composites with regard to

enhancement of their thermal, mechanical, electrical, morphological, and surface properties for potential future applications.

2. Experimental section

2.1. Materials

Phenyltrimethoxysilane (Shin Etsu, 98%), 3-methacryloxypropyltrimethoxysilane (Shin Etsu, 98%), and THF (J.T. Baker, HPLC grade) were vacuum distilled over calcium hydride before use. Potassium carbonate (Dae Jung, 99.8%) was dried in a vacuum oven at 40 °C overnight before use. Photoinitiator Irgacure 184 (BASF), DMF (Sigma Aldrich), PVDF (Solvay, Solef 1010) were used as received.

2.2. Characterization

Weight averaged molecular weight (M_w) and molecular weight distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with refractive index detector (RI-2031 plus), UV detector ($\lambda = 254$ nm, UV-2075 plus), and Viscotek SLS apparatus using THF as the mobile phase at 40 °C with a flow rate of 1 mL/min. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, KF-805). ^1H NMR, ^{29}Si NMR spectra were recorded in CDCl_3 at 25 °C on a Varian Unity INOVA (^1H : 300 MHz, ^{29}Si : 59.6 MHz). FT-IR spectra were measured using Perkin–Elmer FT-IR system (Spectrum-GX) using solvent cast films on KBr pellets. Thermal gravimetric analysis (TGA) was performed by TA Instrument TGA 2950 under N_2 . Differential scanning calorimetry (DSC) was performed by TA Instrument Q20 under N_2 . Nanoindentation measurements were conducted on a Hysitron Inc. TriboIndenter equipped with a Berkovich diamond tip. Measurements of elastic modulus were performed as a continuous stiffness measurement on LPSQ samples coated on silicon wafers at thickness of 20 μm . UV-curing was conducted on a Hitachi UV spot cure system with a total UV energy output of 3 J/cm^2 . WAXD experiments were conducted at the 4C line of the Pohang Accelerator Laboratory (PAL). Dielectric constant was measured using a HP 4192A impedance/gain-phase analyzer applied with HP–Agilent 16451B accessory in the frequency range from 1 kHz to 1000 kHz. The surface contact angle was measured by contact angle analyzer GSA. The surface morphologies were investigated by SEM Inspect F50.

2.3. Synthesis of LPMASQ

In a 100 mL round-bottomed flask, deionized water (2.4 g, 0.133 mol) and potassium carbonate (K_2CO_3) (0.02 g, 0.145 mmol) were charged and stirred for 10 min. Dry THF (4 g, 0.056 mol) was added and stirred for additional 30 min. Afterwards, methacryloxypropyltrimethoxysilane (16 mmol, 3.97 g) and phenyltrimethoxysilane (24 mmol, 4.76 g) monomer mixtures were added dropwise via syringe under nitrogen and the reaction kept for stirring at room temperature for 96 h. Afterwards, the crude reaction mixture was divided into two phases as colorless and cloudy phases. Crude, viscous products were obtained by decantation of the colorless mixed solvent, which was extracted with MC and deionized water several times. After collection of the organic layers, drying over anhydrous magnesium sulfate, filtering, and evaporation of the volatiles, LPMASQ was obtained as a white powder.

2.4. Fabrication of PVLPMMA composites

In a clean glass vial, various weight percentages of PVDF/LPMASQ powders were weighed, and dissolved in DMF to make the

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