



# Segmental dynamics and rheology of miscible poly(vinylidene fluoride)/poly(methyl methacrylate) (70/30 by weight) blend filled with titania or poly(methyl methacrylate)-grafted titania

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## ABSTRACT

Titania (TiO<sub>2</sub>) or poly (methyl methacrylate) (PMMA)-grafted titania (TiO<sub>2</sub>-g-PMMA) were incorporated into miscible poly (vinylidene fluoride) (PVDF)/PMMA (70/30 by weight) blend by melt mixing. TiO<sub>2</sub> particles exhibited aggregation in the composites as displayed by scanning electron microscopy observations and the storage modulus (*G'*) plateau in the low frequency ( $\omega$ ) region. This is accompanied with the restriction of molecular mobility and the elevation of glass transition temperature (*T<sub>g</sub>*). Conversely, TiO<sub>2</sub>-g-PMMA nanoparticles with well-defined cross-linked PMMA shells of 5 nm in thickness are well-distributed in the matrix, without the influence on *T<sub>g</sub>* and the appearance of low- $\omega$  plateau. The dispersion of TiO<sub>2</sub> is not stable during the thermal annealing of the composite in the melt while the TiO<sub>2</sub>-g-PMMA nanoparticles demonstrate excellent dispersion stability. Broadband dielectric spectroscopies indicate that TiO<sub>2</sub> influenced the molecular relaxations of  $\alpha_a$  and  $\alpha_c$ , while the effect of TiO<sub>2</sub>-g-PMMA was negligible. Furthermore, the core-shell structured TiO<sub>2</sub>-g-PMMA nanoparticles produced considerable smaller interfacial polarization than TiO<sub>2</sub> in the composites.

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## 1. Introduction

Semicrystalline poly(vinylidene fluoride) (PVDF) has excellent film-forming ability and mechanical properties. PVDF also has very good resistance to chemicals, oxidation, UV radiation and fungi [1,2]. However, the low surface tension exhibited by PVDF films limits their applications [3]. PVDF is usually blended with oxygen-containing polymers such as poly(methyl methacrylate) (PMMA) to improve processability [4] and endow blends with the desired properties [5,6]. PVDF and PMMA are completely miscible in the melt that results from the specific interaction between the oxygen atom of carbonyl groups of PMMA and the hydrogen atom of PVDF. The blends exhibit a lower critical solution temperature (LCST) of approximately 330 °C [7,8]. PMMA at a content lower than 40% could reduce the crystallinity and yield strength [9] and improve the relative wear rate of the blends [10].

Inorganic particles such as titania (TiO<sub>2</sub>) [11], silica (SiO<sub>2</sub>) [12–14], alumina (Al<sub>2</sub>O<sub>3</sub>) [15,16], calcium carbonate (CaCO<sub>3</sub>) [17], ferroferric oxide (Fe<sub>3</sub>O<sub>4</sub>) [18] and graphene [19] have been extensively used to prepare PVDF composites. However, TiO<sub>2</sub> has received significant attention because of its self-cleaning and discoloration properties under UV light. TiO<sub>2</sub> could improve the mechanical resistance, hydrophilicity, permeability, and the softening temperature of PVDF [20], and affect the crystallization without altering the crystal type [21]. Nano-sized particles could also remarkably improve the antifouling property of PVDF film [11]. However, the aggregation of TiO<sub>2</sub> particles at high concentrations results in the decline of hydrophilicity and permeability [22]. TiO<sub>2</sub> was also applied to improve the mechanical performance in terms of strength and elongation at failure [23] and thereby broadened the application of PVDF/PMMA blend film [24]. PVDF/PMMA/TiO<sub>2</sub> blown films exhibit good mechanical properties, adhesion capability and long-lasting hydrophilicity [25]. For the melt-extruded PVDF/PMMA/TiO<sub>2</sub> (65/20/15) composite films, a  $\alpha$  to  $\beta$  crystal transformation was observed as the casting temperature was increased [26]. Cui et al. [27] found that PMMA grafted TiO<sub>2</sub> (PMMA-g-TiO<sub>2</sub>) by atom transfer radical polymerization could reduce the crystallinity of PVDF and improve the ionic conductivity

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**Table 1**  
Typical recipe for synthesizing TiO<sub>2</sub>-g-PMMA core–shell nanoparticles by seeded emulsion polymerization.

Component	Amount (g)	Concentration (wt%)
deionized water	200	81.1 <sup>a</sup>
MMA	40	16.2 <sup>a</sup>
TiO <sub>2</sub> -γ-MPS	5	2 <sup>a</sup>
SDS	1.2	0.6 <sup>b</sup>
K <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	0.2	0.05 <sup>c</sup>
DVB	0.2	0.05 <sup>c</sup>

<sup>a</sup> Based on total weight.

<sup>b</sup> Based on weight of aqueous phase.

<sup>c</sup> Based on monomer weight.

and electrochemical stability. Zhao et al. [28] prepared the composites with enhanced hydrophilicity by adding TiO<sub>2</sub> or SiO<sub>2</sub> nanoparticles during *in situ* polymerization of methyl methacrylate (MMA) in PVDF solution. However, rheology and molecular relaxation of PVDF/PMMA/TiO<sub>2</sub> composite in the molten state are rarely investigated, even though they are quite important for processing multicomponent composites exhibiting optimal performance.

The influence of nanoparticles on the phase separation and final morphology of miscible polymer blends has attracted considerable attention over the decades [29–32]. Nano-fillers may either increase or decrease the interaction parameters between two polymeric components. This changes the phase stability and affects the kinetics of phase separation [33–38]. However, the effect of the aggregation of nanoparticles due to thermal treatment is almost ignored despite intensive studies of the thermodynamics of phase separation. To a large extent, the performance improvement of polymer composites depends on the filler dispersion and the interfacial bonding between the filler particles and the polymer matrix. Therefore, time scanning rheology is applied to the filled miscible PVDF/PMMA (70/30 by weight) blend in the homogeneous regime far below LCST for illustrating the filler aggregation during processing. The core–shell structured TiO<sub>2</sub>-g-PMMA nanoparticles prepared via seeded emulsion polymerization are incorporated into the blend by melt blending. The effect of virgin TiO<sub>2</sub> and TiO<sub>2</sub>-g-PMMA on dielectric and rheological properties of the composites is investigated. Furthermore, the glass transition and crystallization behaviors of the composites in the semicrystalline state are also investigated.

## 2. Experimental

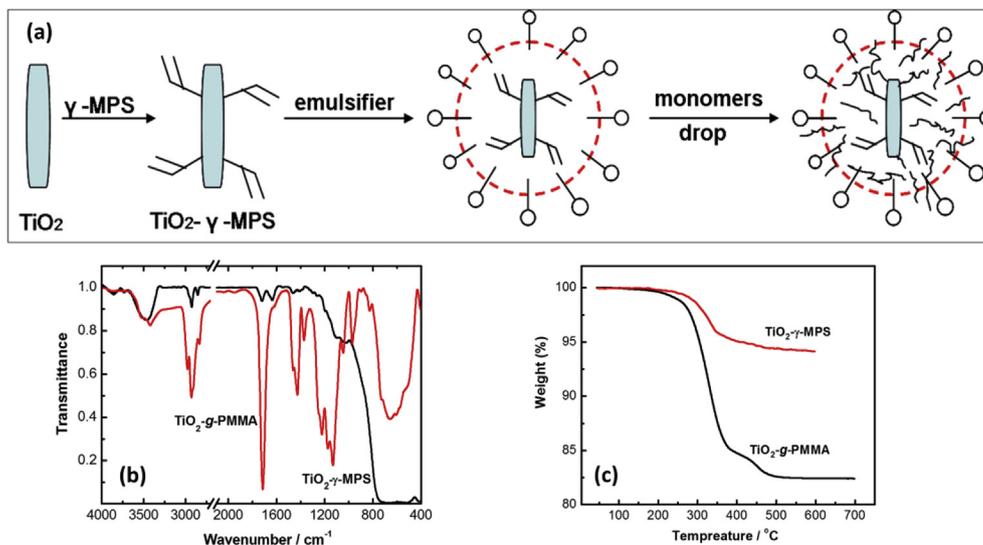
### 2.1. Materials

PVDF (FR906,  $M_w = 20.7 \times 10^4$ ,  $M_w/M_n = 2.61$ , melting point: 168 °C) and PMMA (IF850,  $M_w = 8.6 \times 10^4$ ,  $M_w/M_n = 2.04$ ) resins in pellet form were obtained from Shanghai 3F New Mater. Co., China and LG Co., Korea, respectively. Rutile TiO<sub>2</sub> nanoparticles with the size of 100–200 nm were purchased from Hangzhou Wanjing New Mater. Co., China. Antioxidant (At 10) was provided by Virtulla Tianjin Techn. Co., China. Coupling agent γ-methacryloxypropyl trimethoxysilane (γ-MPS), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), and divinyl benzene (DVB) were from Aladdin Reagent Inc., China. Methyl methacrylate (MMA), sodium hydroxide (NaOH), sodium dodecyl sulfate (SDS), ethanol, and toluene of analytical purity were provided by Sinopharm Chem. Reagent Co., China. MMA monomer was purified with 5% NaOH solution and washed for five times by deionized water.

### 2.2. Synthesis of TiO<sub>2</sub>-g-PMMA core–shell nanoparticles

The TiO<sub>2</sub> powder pretreated at 400 °C for 4 h was mixed with a certain amount of γ-MPS in 300 ml toluene that was in a 500 ml three-neck flask equipped with a condenser. The suspension was mechanically stirred in an oil bath for 12 h at 110 °C. The γ-MPS modified TiO<sub>2</sub> (TiO<sub>2</sub>-γ-MPS) was obtained by centrifugation at 6000 rpm for 15 min and then re-dispersed in ethanol with four times. The deposit was dried to a state of constant weight at 70 °C in vacuum for 24 h.

TiO<sub>2</sub>-g-PMMA core–shell nanoparticles were fabricated via seeded emulsion polymerization with a recipe given in Table 1 and a synthesis process shown in Fig. 1a. SDS, K<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, DVB, and TiO<sub>2</sub>-γ-MPS were added in deionized water in a 500 ml four-neck round-bottom flask equipped with a poly(tetrafluoroethylene) coated stir bar. The mixture was mechanically stirred for 30 min at ambient temperature, while under N<sub>2</sub> purging. Within one hour of the temperature rising to 70 °C, MMA monomer was dropped into the reactor by a dropping funnel. After 8 h of emulsion polymerization with TiO<sub>2</sub>-γ-MPS as the seeds of polymerization, the product was demulsified and purified by centrifugation and re-dispersed in toluene for four times to remove any free polymer. The undissolved nanoparticles were collected and dried at 70 °C in vacuum for 24 h.



**Fig. 1.** (a) Schematic for synthesis of TiO<sub>2</sub>-g-PMMA by seeded emulsion polymerization, (b) FTIR spectra and (c) TGA curves of TiO<sub>2</sub>-γ-MPS and TiO<sub>2</sub>-g-PMMA.

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