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Photocatalytic activity of vinylidene fluoride-containing copolymers/anatase titanium oxide/silica nanocomposites



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ABSTRACT

A series of three fluorinated copolymers (FP) based on vinylidene fluoride (VDF) were involved in the preparation of original FP/anatase titanium oxide (*an*-TiO₂), and FP/silica/*an*-TiO₂ nanocomposites. These FP copolymers were prepared by conventional free radical copolymerization of VDF with various functional fluorinated comonomers such as F₂C=CFCO₂Me, FCH=CFCO₂H, and F₂C=CFCH₂COCH₃ in good yields (>60%) and had number average molecular weights of ca. 50,000 g mol⁻¹. Anatase titanium oxide in the FP/*an*-TiO₂ nanocomposites underwent an effective modification into rutile polymorphism after calcination at 1000 °C. Although the parent *an*-TiO₂ nanoparticles changed completely into rutile nanoparticles after calcination at 1000 °C, *an*-TiO₂ embedded in the FPs/silica/*an*-TiO₂ nanocomposites retained their structures without any phase transformation into rutile, due to locking the Ti–O species at the interface of TiO₂ domains by the Ti–O–Si units, whose lattice can be formed by the interaction of silica with *an*-TiO₂ nanoparticles. Even after such a thermal treatment, these nanocomposites displayed a higher photocatalytic activity for the discoloration of methylene blue as well as those of the corresponding nanocomposites before calcination, although the original *an*-TiO₂ nanoparticles could not exhibit a photocatalytic ability after calcination. Among these nanocomposites based on VDF-containing copolymers, poly(VDF-*co*-CF₂CFCO₂CH₃)/SiO₂/*an*-TiO₂ before and after calcination displayed better photocatalytic properties than those of the other FP nanocomposites. More interestingly, this FP/silica/*an*-TiO₂ nanocomposite even after calcination at 1000 °C was able to preserve the same photocatalytic activity as that before calcination. In addition, these FP/TiO₂ and FP/SiO₂/TiO₂ composites exhibited high thermal stability up to 800 °C with a loss weight of 2% (or ca. 14% for the acidic FP) only.

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1. Introduction

Titanium oxide (TiO₂) is the most important white pigment involved in coating and plastic industry because

of the high refractive index of TiO₂ nanoparticles ($n_D \sim 2.6$), which enables it to produce high gloss composites [1]. It is widely used because it efficiently scatters visible light, thereby imparting whiteness, brightness, and opacity when incorporated in coatings, as well as in cosmetics and toothpastes. It has been utilized in many applications ranging from photocatalysis [2], catalyst supports [3], dye-sensitized solar cells [4], semiconductors

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and capacitors [5], photovoltaics [6], ductile ceramics [7], lithium ion batteries (LIB) [8] (especially anatase, rutile TiO_2 and $\text{TiO}_2(\text{B})$ polymorphs are promising structures for anode materials in LIB), and to gas sensors [9]. In addition, organic polymer matrices containing dispersed TiO_2 oxide nanoparticles have found a practical use for mediating photochemical process in membranes, catalytic sensors, and photosensitive materials and for stimulating numerous biochemical and biophysical process [10,11]. However, the dispersion of the nanoparticles uniformly throughout organic polymeric matrices is an issue, because the nanoparticles can easily agglomerate or coalesce forming large particles which result in a reversed effect on the catalyst efficiency [12,13]. In their comprehensive review, Fröschl et al. [5] reported selective synthetic methods towards TiO_2 nano-materials and these authors mentioned that TiO_2 displays various phases: amorphous, rutile, anatase and brookite. The last one has been involved in various applications, especially for electrochemical Lithium insertion [14]. A few polymer/ TiO_2 composites have been reported in the literature, for example by Thomas et al. [15–18] who used isotactic polystyrene [15], natural rubber–EPDM [16], nitrile rubber [17], and also synthesized natural rubber/nano $\text{SiO}_2/\text{TiO}_2$ composites [18]. In addition, Chu et al. [19] described original PEO-*b*-PPO-*b*-PEO triblock copolymer/ TiO_2 composites. As a matter of fact, fluorinated polysoaps are well-known to exhibit a superior surface active property than that of the corresponding non-fluorinated homologs [20,21]. Thus, it was of particular interest to develop fluorinated polymers/ TiO_2 nanocomposites that possess satisfactory dispersibility and stability. Actually, only a few publications focus on the fluoropolymers/ TiO_2 composites based on poly(tetrafluoroethylene), PTFE [22], poly(vinylidene fluoride), PVDF [23], poly(fluoroacrylate)s [24], fluoroalkyl end capped polymers (that displayed good dispersibility and stability in various solvents) [25], fluoroalkyl end-capped vinyltrimethoxysilane oligomer [26], poly(TFE-*co*-HFP) copolymer [27], and poly(VDF-*co*-TrFE) copolymer [28] (where HFP and TrFE stand for hexafluoropropylene and trifluoroethylene, respectively). In addition, anatase titanium oxide (*an*- TiO_2) seems to behave as a more efficient photocatalyst than the rutile one. However, *an*- TiO_2 can be irreversibly modified into rutile *an*- TiO_2 at elevated temperatures [29–31]. Concerning the thermally stable TiO_2 nanocomposites for various applications, it was worth exploring new fluorinated (co)polymers/*an*- TiO_2 nanocomposites that possess not only a good dispersibility in solvents as well as satisfactory chemical and thermal stabilities but also a higher photocatalytic activity without any phase transformation into rutile under higher temperature conditions. It has been hitherto reported that the fluorination of TiO_2 , involving either fluorine adsorption or lattice fluorine-doping, is effective for the enhancement of the photocatalytic activity of TiO_2 [32–36], compared to that of the original TiO_2 . Therefore, it is expected that reactions of *an*- TiO_2 nanoparticles with fluorinated polymers to generate original composites should enhance the photocatalytic property of *an*- TiO_2 in the resulting fluorinated copolymers/ TiO_2 composites. The present study attempts to investigate if fluorinated

copolymers may enhance not only the photocatalytic ability of *an*- TiO_2 but also the thermal stability of these fluorinated copolymers through reactions of these corresponding copolymers with *an*- TiO_2 nanoparticles and SiO_2 nanoparticles. In particular, it was of interest to investigate if original resulting fluorinated copolymers/silica/*an*- TiO_2 nanocomposites could enable to preserve the *an*- TiO_2 structure after calcination at 1000 °C and display a good photocatalytic activity imparted by such a nanofiller within the composites. These are the objectives of this present study.

2. Experimental

2.1. Materials

Titanium oxide nanoparticles (average particle size: 20 nm) were received from Ishihara Sangyo Kaisha Ltd. (Osaka, Japan). Vinylidene fluoride (VDF) copolymers, poly(VDF-*co*- $\text{CF}_2\text{CFCO}_2\text{CH}_3$) [37], poly(VDF-*co*- $\text{CFHCFCO}_2\text{H}$) [38], and poly(VDF-*co*- $\text{CF}_2\text{CF}(\text{CH}_2)_3\text{OCOCH}_3$) [39] copolymers were prepared by reported methods of conventional free radical copolymerizations of vinylidene fluoride (VDF) with $\text{F}_2\text{C}=\text{CO}_2\text{CH}_3$, $\text{FCH}=\text{CFCO}_2\text{H}$, and $\text{F}_2\text{C}=\text{CF}(\text{CH}_2)_3\text{OCOCH}_3$ comonomers, respectively. Their molecular weights (assessed by size exclusion chromatography, Figs. S1–S3 in the Supporting Information) were ca. 50,000 g mol^{−1} (with poly(methyl methacrylate), PMMA standards) while their microstructures (i.e. the mol. contents of VDF and fluorinated functional comonomers in the copolymers) were determined by ¹⁹F NMR spectroscopy, supplied in Fig. 1 and in Figs. S4 and S5.

2.2. Analytical techniques

Molecular weights of VDF copolymers were assessed at 40 °C by using SEC with columns 2HR5E and 1HR2E types with DMF/LiBr in 0.1 mol l^{−1} as the eluent with an isocratic pump and PMMA standards. Dynamic light-scattering (DLS) measurements were carried out using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Field emission scanning electron micrographs (FE-SEM) and energy dispersive X-ray (EDX) spectra were obtained using JEOL JSM-7000F (Tokyo, Japan). X-ray diffraction (XRD) measurements were performed by the use of Mac Science M18XHF-SRA (Tokyo, Japan). ¹H NMR spectra were recorded using JEOL JNM-400 (400 MHz) FT NMR SYSTEM (Tokyo, Japan). ¹⁹F NMR spectra were recorded on Bruker AC 400 instruments in DMF-*d*₇ with CFCl_3 as the reference. The experimental conditions for recording ¹H (or ¹⁹F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 512, and 1024 for ¹³C NMR), and a pulse width of 5 μs for ¹⁹F NMR.

Thermal analyses were carried out by raising the temperature up to around 800 °C, at a heating rate of 10 °C min^{−1}, under air atmospheric conditions, by the use of Bruker axs TG-DTA2000SA differential thermobalance (Kanagawa, Japan).

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