Colloid Polym Sci (2007) 285:499–506
DOI 10.1007/s00396-006-1566-8

ORIGINAL CONTRIBUTION

Preparation and applications of novel fluoroalkyl end-capped oligomers/calcium carbonate nanocomposites

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Received: 19 May 2006 / Accepted: 22 August 2006 / Published online: 9 November 2006

Abstract Calcium chloride reacted with sodium carbonate in the presence of a variety of self-assembled molecular aggregates formed by fluoroalkyl end-capped acrylic acid, 2-methacryloyloxyethane sulfonic acid, dimethylacrylamide, and acryloylmorpholine oligomers in aqueous solutions to afford the corresponding fluorinated oligomers/calcium carbonate composites in excellent to moderate isolated yields. These fluorinated calcium carbonate composites thus obtained were shown to have a good dispersibility not only in water but also in traditional organic media including fluorinated solvents. Dynamic light scattering measurements (DLS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that these fluorinated composites are nanometer-size-controlled particles and well dispersed in these media. Cross-linked fluoroalkyl end-capped acrylic acid co-oligomer containing poly(oxyethylene) units was also applied to the preparation of new cross-linked fluorinated calcium carbonate nanocomposites under similar conditions. The obtained cross-linked fluorinated calcium carbonate nanocomposites were found to have an extremely higher dispersibility in aqueous and organic media including fluorinated solvents, compared to that of the corresponding fluoroalkyl end-capped oligomer nanocomposites. In particular, it was verified that these fluorinated calcium carbonate nanocomposites are applicable to the dispersion above poly (methyl methacrylate) (PMMA) film surface. Interestingly, field-emission SEM (FE-SEM) images of the cross-section of the modified PMMA films showed that calcium carbonate particles dispersed into these PMMA films could be arranged regularly above the modified film surface. More interestingly, cross-linked fluorinated oligomeric aggregates were able to provide suitable host moieties for the crystallization of calcium carbonate.

Keywords Calcium carbonate · Nanocomposites · Fluorinated oligomer · Cross-linked aggregate · Dispersion · Molecular aggregate · Surface modification

Introduction

Hitherto, there has been an attracted great interest in organic–inorganic nanocomposites, because the nanocomposites could exhibit combined properties of both organic molecules and inorganic nanoparticles [1–4]. In particular, these nanocomposites could dramatically induce an improvement in mechanical and electrical properties, heat resistance, radiation resistance, and other properties as a result of the nanometer-size dispersion of the inorganic fillers in the organic matrix [1–4]. Calcium carbonate is a cheap, commercially available inorganic particle, and has been widely used as an inorganic filler in the manufacture of paint, paper, rubber and plastics, and the production of toothpaste, and binding agents [5, 6]. Usually, the micrometer-size commercially available calcium carbonates have been used to merely reduce the cost of expensive resins; however, the improvement in the various properties such as mechanical property of micrometer-size calcium carbonate-filled composites is believed to be poor due to the decrease of the polymer–filler interaction [7]. Thus, the preparation of nanocomposite particles by the encapsulation of calcium carbonate particles into organic polymers is an efficient method to prevent the agglomeration and improve a variety

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of properties such as mechanical and electrical properties, heat resistance, and radiation resistance of the parent polymers.

In fact, there have been numerous reports on the encapsulations of calcium carbonate into organic polymers, including their applications [8–17]; however studies on the development of calcium carbonate–polymers nanocomposites, which could exhibit a good dispersibility into a variety of solvents, have been very limited, although these studies have been the subject of considerable research of a fundamental and applied nature. On the other hand, it is well-known that fluorinated polymers such as poly(tetrafluoroethylene) are functional materials due to their exhibited excellent chemical and thermal stability, low surface energy, and low refractive index and dielectric constant [18, 19]. In these fluorinated polymers, partially fluoroalkylated oligomers, in particular fluoroalkyl end-capped oligomers, are attractive functional materials, because they exhibit various unique properties such as high solubility, surface-active properties, biological activities, and nanometer-size-controlled self-assembled molecular aggregates, which cannot be achieved by the corresponding non-fluorinated, randomly or block-type fluoroalkylated polymers, and low-molecular weight fluorinated surfactants [20, 21]. From the developmental viewpoints of novel calcium carbonate nanocomposites, it is of particular interest to prepare fluorinated calcium carbonate nanocomposites that could exhibit not only surface-active properties but also colloidal dispersibility and stability into a variety of solvents imparted by fluorine, by the use of fluoroalkyl end-capped oligomer as a key intermediate.

Now, we have found that a variety of fluoroalkyl end-capped oligomers/calcium carbonate nanocomposites can be prepared by the reactions of calcium chloride with sodium carbonate in the presence of nanometer-size-controlled fluorinated molecular aggregates formed by fluoroalkyl end-capped oligomers to exhibit a good dispersibility not only in water but also in organic media including fluorinated aliphatic solvents. These fluorinated oligomers/calcium carbonate nanocomposites were applied to the surface modifications of traditionally organic polymers such as poly(methyl methacrylate) to exhibit a good surface-active characteristic imparted by fluorine on their surface. More interestingly, these new fluorinated nanocomposites were found to be a convenient tool for the arrangements of calcium carbonate nanoparticles above the PMMA surface. These results will be described herein.

Results and discussion

Sodium carbonate reacted smoothly with calcium chloride in the presence of fluoroalkyl end-capped acrylic acid oligomer [R_F-$(ACA)_n$-R_F; R_F=$CF(CF_3)OC_3F_7$; Mn=2770] in aqueous solutions at room temperature to afford fluoroalkyl end-capped acrylic acid oligomer/calcium carbonate nanocomposites in 58% isolated yield. Other fluoroalkyl end-capped oligomers were also found to afford the corresponding fluorinated oligomers/calcium carbonate nanocomposites in excellent to moderate isolated yields under similar conditions. These results were demonstrated in Scheme 1 and Table 1.

As shown in Scheme 1 and Table 1, not only fluorinated acrylic acid oligomers but also fluorinated sulfonic acid oligomer [R_F-$(MES)_n$-R_F], dimethylacrylamide oligomer [R_F-$(DMAA)_n$-R_F], and acryloylmorpholine oligomer [R_F-$(ACMO)_n$-R_F] were able to afford the fluorinated oligomers/calcium carbonate nanocomposites in 45~65% isolated yields. Elementary analyses of fluorine and FT-IR analyses for the calcium carbonate nanocomposites thus obtained showed the presence of fluoroalkyl end-capped oligomers in the composites.

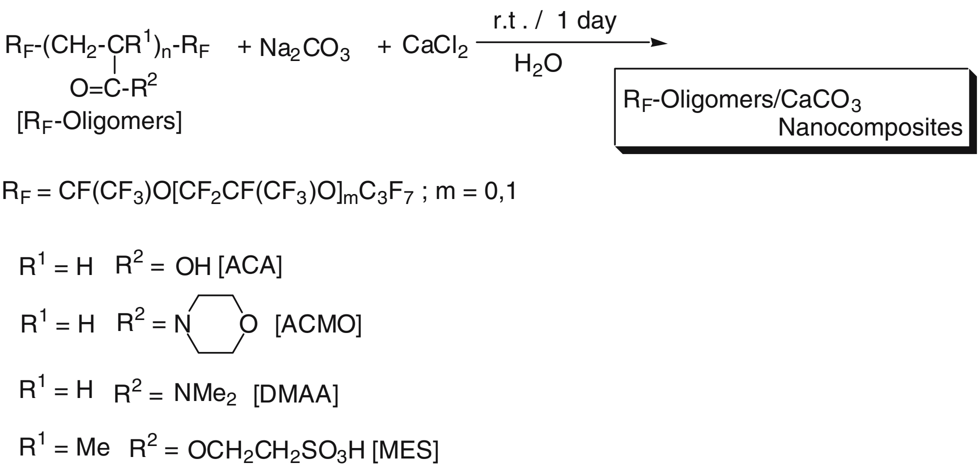
The contents of fluorinated oligomers in the composites were also estimated by the use of TGA, in which the weight loss of this composite was measured by raising the temperature to around 800 °C. The thermal stability of each fluorinated calcium carbonate nanocomposite was found to decrease significantly compared to that of the parent calcium carbonate. The contents of fluorinated oligomers in the composites were estimated to be 7~22%, in comparison with the parent calcium carbonate, and these results are also shown in Table 1.

Interestingly, each fluorinated calcium carbonate nanocomposite (2 g/dm^3) in Table 1 were found to exhibit a good dispersibility not only in water but also in common organic solvents such as 1,2-dichloroethane, tetrahydrofuran, and methanol including fluorinated aliphatic solvents (AK-225:1:1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane). Especially, these fluorinated calcium carbonate nanocomposites were found to exhibit a higher dispersibility in fluorinated solvents (AK-225), indicating that van der Waals interactions between fluoroalkyl segments in fluorinated nanocomposites and the fluorinated solvents are essential for a higher dispersibility.

We have measured the size of fluoroalkyl end-capped oligomers/calcium carbonate nanocomposites in aqueous solutions by dynamic light-scattering (DLS) measurements (DLS-6000 HL: Otsuka Electronics, Japan) at 30 °C. The size of the parent fluoroalkyl end-capped oligomeric aggregates was also measured under similar conditions for comparison. These results are shown in Table 2.

As shown in Table 3, the size (22~62 nm: number-average diameter) of fluorinated calcium carbonates nanocomposites was increased by the composite reactions of calcium carbonate with fluoroalkyl end-capped oligomers,

Scheme 1 Fluorinated oligomers/calcium carbonate nanocomposites



compared to that (11 nm) of the parent fluoroalkyl end-capped oligomeric aggregates. The increase of the size of nanoparticles indicates that the composite reactions of calcium carbonate with fluoroalkyl end-capped oligomers could proceed smoothly to afford fluorinated calcium carbonate composite nanoparticles with around 22~62 nm size levels through the encapsulation of calcium carbonate nanoparticles into the fluoroalkyl end-capped oligomeric aggregate cores. Interestingly, a variety of isolated fluorinated calcium carbonate nanocomposite powders were found to exhibit a good redispersibility in water. The size (37~178 nm) of the redispersed fluorinated particles did not change so much even after the redispersion of the parent fluorinated particle powders into water (see Table 2), and the size of each particle showed a monodispersed characteristic.

We have measured scanning electron micrograph (SEM) and transmission electron micrograph (TEM) photographs of methanol solutions of R_F-(MES)$_n$-R_F/calcium carbonate nanocomposites [R_F=CF(CF$_3$)OC$_3$F$_7$], and the results are shown in Figs. 1 and 2.

The electron micrographs (SEM and TEM) also showed the formation of fluorinated calcium carbonate composite nanoparticles with a mean diameter of 806 and 468 nm, respectively. The difference in the average sizes determined by DLS and SEM (or TEM) (DLS ~45 nm, SEM ~806 nm, TEM ~468 nm) would be due to the coagulation or agglomeration of the nanoparticles during sample preparations for SEM and TEM measurements.

To develop new fluorinated calcium carbonate nanocomposites, which possess a superior dispersibility into a variety of solvents compared to the fluoroalkyl end-capped oligomer nanocomposites, it is very interesting to study on the preparation of calcium carbonate nanocomposites by the use of cross-linked fluoroalkyl end-capped oligomeric nanoparticles. Cross-linked fluorinated oligomeric nano-

Table 1 Preparation of fluoroalkyl end-capped oligomers [R_F-oligomers]/$CaCO_3$ nanocomposites and contents of R_F-oligomers in R_F-oligomers/$CaCO_3$ nanocomposites determined by TGA

Run	R_F oligomers (R_F in oligomer) [Mn] (mg)	Na_2CO_3 (mmol)	$CaCl_2$ (mmol)	Products Yield[a] (%)	Contents of R_F-oligomers in nanocomposites (%)
1	R_F-(ACA)$_n$-R_F R_F=CF(CF$_3$)OC$_3$F$_7$ [2,770] (56)	1.0	1.0	58	22
2	R_F=CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ [3,740] (56)	1.0	1.0	62	12
3	R_F-(MES)$_n$-R_F R_F=CF(CF$_3$)OC$_3$F$_7$ [13,700] (84)	1.0	1.0	45	7
4	R_F-(ACMO)$_n$-R_F R_F=CF(CF$_3$)OC$_3$F$_7$ [8,820] (56)	1.0	1.0	64	8
5	R_F-(DMAA)$_n$-R_F R_F=CF(CF$_3$)OC$_3$F$_7$ [4,820] (56)	1.0	1.0	65	11

[a] The yield was based on R_F-oligomer and $CaCO_3$ (1.0 mmol)

Table 2 Size of R_F-oligomers/$CaCO_3$ nanocomposites [R_F=CF(CF_3)OC_3F_7] in aqueous solutions determined by dynamic light scattering measurements

Run[a]	R_F-oligomer/ $CaCO_3$ nanocomposites	Size of dispersed particles (nm)	Size of redispersed particles (nm)
1	R_F-(ACA)$_n$-R_F [10.7±1.1][b]	62.1±11.3	178.3±24.3
3	R_F-(MES)$_n$-R_F [10.8±1.1][b]	51.2±0.0	37.2±4.0
4	R_F-(ACMO)$_n$-R_F [10.9±1.3][b]	36.3±9.9	47.5±10.5
5	R_F-(DMAA)$_n$-R_F [10.5±1.5][b]	21.9±5.2	78.8±15.4

[a] Each one is different from those of Table 1.

[b] Size of the corresponding parent R_F-oligomeric aggregates

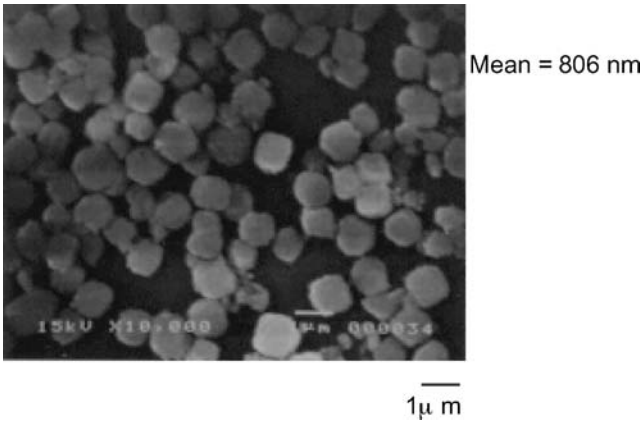


Fig. 1 SEM images of methanol solutions of R_F-(MES)$_n$-R_F/CaCO3 nanocomposites [R_F=CF(CF_3)OC_3F_7]

particles are built up through the more fixed nanometer-size oligomeric aggregates cores compared to the corresponding fluorinated oligomeric cores formed by the aggregation between the end-capped fluoroalkyl segments in oligomers. Calcium carbonate nanoparticles should be more tightly encapsulated into the cross-linked fluorinated aggregate cores to exhibit an excellent dispersibility into a variety of solvents. Thus, we tried to prepare new fluorinated calcium nanocomposites by the use of cross-linked fluorinated co-oligomer [R_F-(PDE-100)$_x$-(ACA)$_y$-R_F], which was obtained by the reaction of fluoroalkanoyl peroxide with dimethacrylate monomer containing poly(oxyethylene) units [PDE-100: CH_2=CMeC(=O)O(CH_2CH_2O)$_2$C(=O)CMe=CH_2] and acrylic acid [ACA: CH_2=CHCOOH] [22–25], and these results were shown in Scheme 2.

As shown in Scheme 2, the expected cross-linked fluorinated calcium carbonate nanocomposite was obtained in 83% isolated yield. The obtained nanocomposite was found to exhibit a remarkably higher dispersibility not only in water but also in common organic solvents including fluorinated solvents such as 1,2-dichloroethane, tetrahydrofuran, methanol and fluorinated solvents (AK-225) in comparison to that of the corresponding fluoroalkyl end-capped oligomer/calcium carbonate nanocomposites. In addition, we have measured the size of cross-linked fluorinated oligomer/calcium carbonate nanocomposites by the dynamic light-scattering measurements. The size of the cross-linked fluorinated oligomeric aggregate was also measured under similar conditions, for comparison. The size (number-average diameter) of cross-linked fluorinated oligomer/calcium carbonate nanocomposites was decreased from 390.5±60.4 nm to 283.2±64.1 nm by the composite reaction of the parent cross-linked fluorinated oligomer with calcium carbonate.

Table 3 Contact angles of dodecane on the modified PMMA films tretaed with R_F-oligomers/$CaCO_3$ nanocmposites [R_F=CF(CF_3)OC_3F_7]

R_F-oligomers/$CaCO_3$ nanocomposites	Contact angle (degree)		
	Surface side	Reverse side	Film thickness (μm)
R_F-(ACA)$_n$-R_F	12	0	194
R_F-(MES)$_n$-R_F	33	6	197
R_F-(PDE-100)$_x$-(ACA)$_y$-R_F	32	9	193

This finding strongly suggests that calcium carbonate nanoparticles should be encapsulated into the nanometer-size-controlled cross-linked fluorinated aggregates cores, and the calcium carbonate-encapsulated fluorinated aggregates cores should shrink in size through the strong interaction between the calcium carbonate particles and carboxy or poly(oxyethylene) units in the fluorinated aggregates cores. SEM and TEM images of freshly prepared calcium carbonate composites by the use of cross-linked fluorinated oligomer in Scheme 2 are well dispersed and very fine particles with average diameters of 693 and 387 nm, respectively (see Figs. 3 and 4), compared to that of R_F-(MES)$_n$-R_F/calcium carbonate nanocomposites in Figs. 1 and 2.

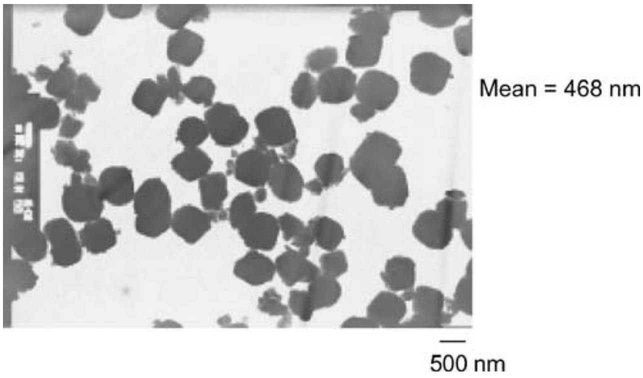
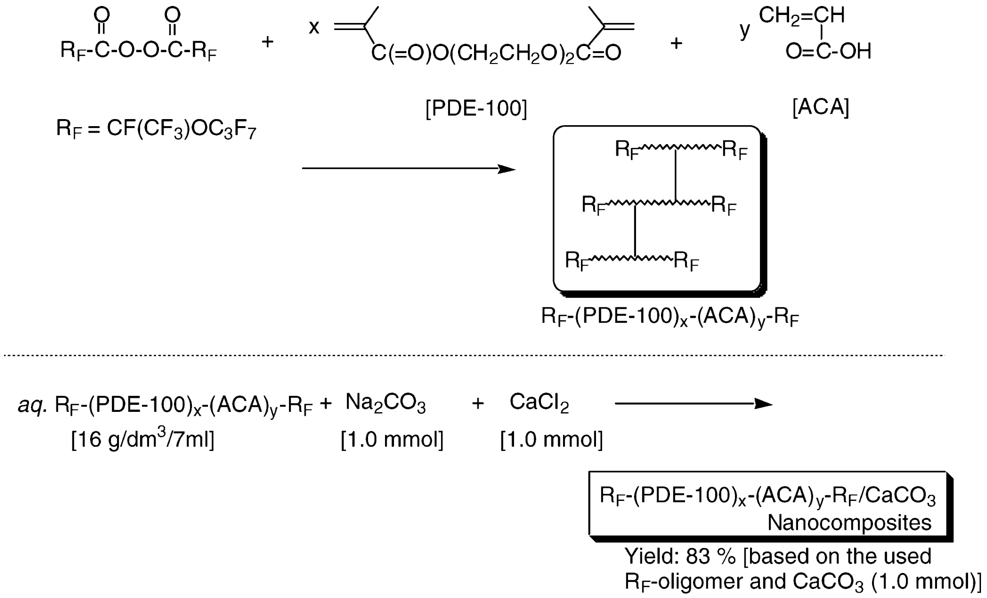


Fig. 2 TEM Image of R_F-(MES)$_n$-R_F/$CaCO_3$ nanocomposites in methanol [R_F=CF(CF_3)OC_3F_7]

Scheme 2 Cross-linked fluorinated cooligomer/calcium carbonate nanocomposites



Therefore, it is very interesting to develop our present very fine fluorinated calcium carbonate nanocomposites to the surface modification for traditional polymeric materials such as poly(methyl methacrylate) (PMMA). We have prepared the cast PMMA films treated with fluorinated calcium carbonate nanocomposites, and the contact angles of dodecane on the modified PMMA films were measured. These results are shown in Table 3.

As shown in Table 3, contact angles of dodecane on the modified PMMA film surface treated with fluorinated composites showed significantly large values (12~33°), respectively, which exhibit a good oleophobicity imparted by fluoroalkyl segments in nanocomposites on the PMMA surface. In contrast, the contact angles of dodecane on the reverse sides were extremely decreased (9~0°), indicating that our present fluorinated nanocomposites can be dispersed regularly on the polymer surface during the cast film formation. Thus, not only fluorinated oligomeric aggregates but also encapsulated calcium carbonate particles should be well dispersed above the polymer surface. In fact, interestingly, field-emission SEM (FE-SEM) images of the cross-section of the modified PMMA films showed that calcium carbonate nanoparticles in the modified PMMA films treated with cross-linked fluorinated co-oligomer composites and R_F-(MES)$_n$-R_F oligomer composites are regularly arranged only above the modified PMMA surface as shown in Figs. 5 and 6, respectively.

More interestingly, it was found that cross-linked fluorinated oligomeric aggregates in the modified PMMA film could afford flat crystals of calcium carbonate into their cores as in Fig. 5, although the corresponding R_F-(MES)$_n$-R_F oligomer nanocomposites were failed to afford such crystals in Fig. 6. XRD analyses of the crystals formed in the cross-linked fluorinated aggregates (see Fig. 7) show that calcite is mainly obtained. In contrast, interestingly, vaterite is mainly obtained in the case of R_F-(MES)$_n$-R_F oligomer nanocomposites (see Fig. 8). Thus, our present cross-linked fluorinated nanocomposites are applicable to a

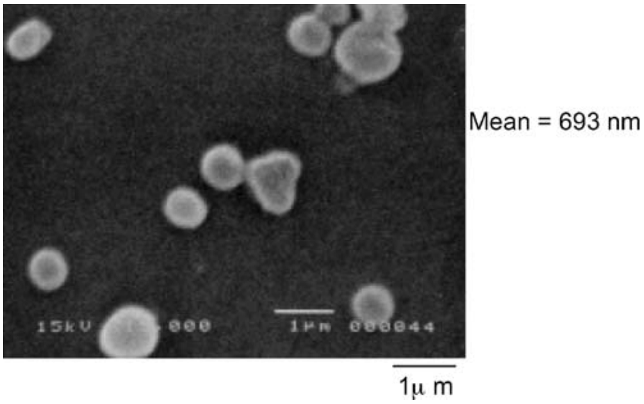


Fig. 3 SEM images of methanol solutions of R_F-(PDE-100)$_x$-(ACA)$_y$-R_F/$CaCO_3$ nanocomposites [R_F=$CF(CF_3)OC_3F_7$]

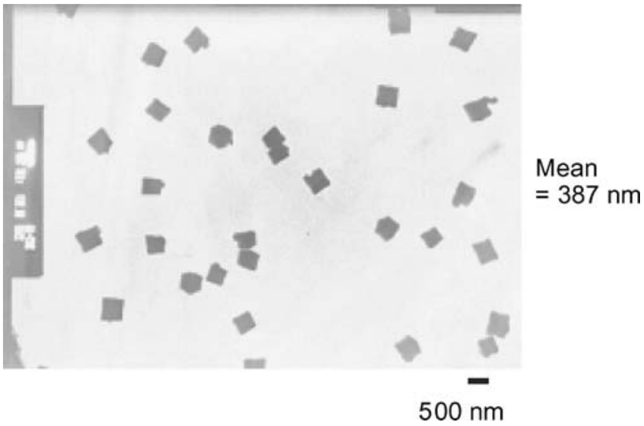


Fig. 4 TEM Image of R_F-(PDE-100)$_x$-(ACA)$_y$-R_F/$CaCO_3$ nanocomposites in methanol [R_F=$CF(CF_3)OC_3F_7$]

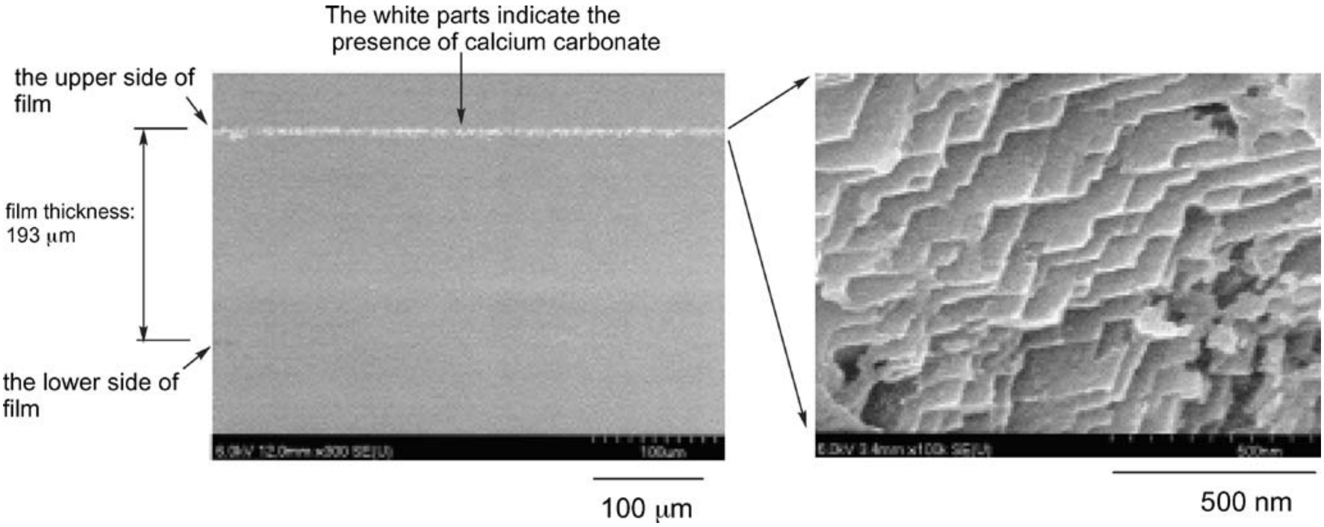


Fig. 5 FE-SEM images of cross-section of the modified PMMA films treated with R_F-(PDE-100)$_x$-(ACA)$_y$-R_F/$CaCO_3$ nanocomposite shown in Scheme 2

novel synthetic approach to the fabrication of composite materials via controlling crystal growth with fluorinated aggregate cores as a template.

In conclusion, we have succeeded in preparing new fluorinated oligomers/calcium carbonate nanocomposites by the reactions of calcium chloride and sodium carbonate in the presence of fluoroalkyl end-capped oligomers. These fluorinated calcium carbonate nanocomposites thus obtained were found to have a good dispersibility in water and a variety of organic solvents including fluorinated aliphatic solvents. We have also prepared cross-linked fluorinated co-oligomer/calcium carbonate nanocomposite by the use of cross-linked fluoroalkyl end-capped acrylic acid co-oligomer containing poly(oxyethylene) units under similar conditions. This cross-linked fluorinated calcium carbonate nanocomposite was found to exhibit a higher dispersibility in aqueous and organic media including fluorinated solvents, compared to that of the corresponding fluoroalkyl end-capped oligomers nanocomposites. A variety of fluorinated calcium carbonate nanocomposites were applied to the dispersion above poly(methyl methacrylate) [PMMA] film surface.

Interestingly, FE-SEM images of the cross-section of the modified PMMA films showed that calcium carbonate particles could be arranged regularly above the modified PMMA film surface. More interestingly, cross-linked fluorinated oligomeric aggregates were able to provide more suitable host moieties for the crystallization of calcium carbonate. Further studies are actively in progress.

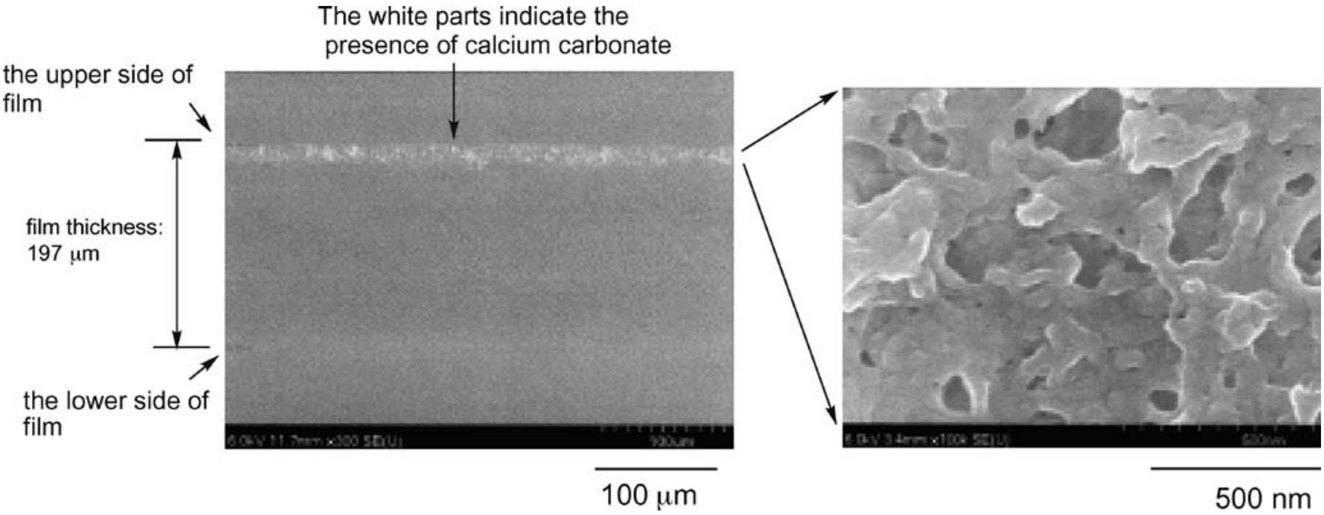


Fig. 6 FE-SEM images of cross-section of the modified PMMA films treated with R_F-(MES)$_n$-R_F/$CaCO_3$ nanocomposite shown in Table 1

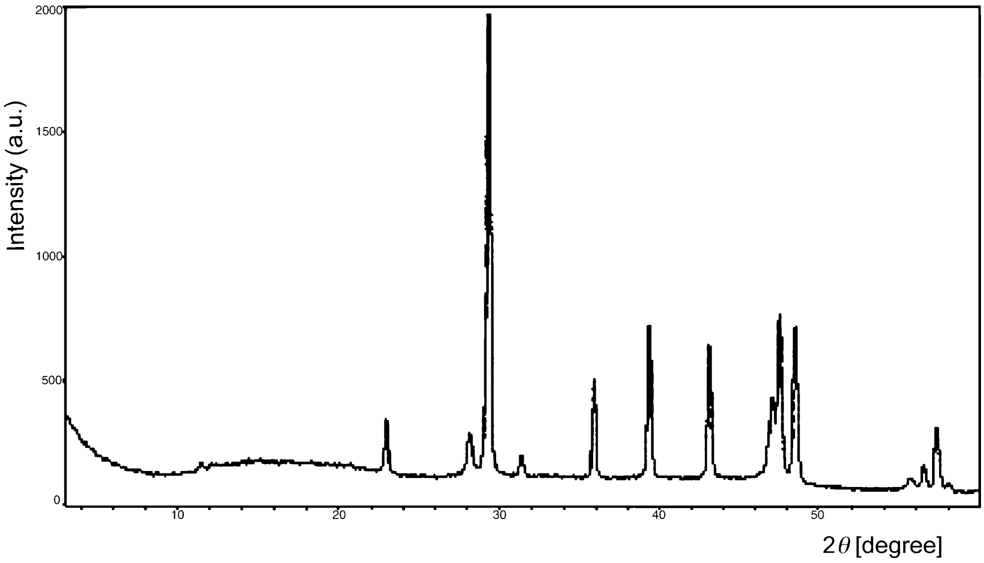


Fig. 7 X-ray diffraction of R_F-$(PDE)_x$-$(ACA)_y$-$R_F/CaCO_3$ nanocomposites

Experimental

A typical procedure for the preparation of fluorinated oligomers–calcium carbonate nanocomposites is as follows: to an aqueous solution of fluoroalkyl end-capped acrylic acid oligomer [R_F-$(CH_2CHCOOH)_x$-R_F: R_F-$(ACA)_n$-R_F; R_F=$CF(CF_3)OC_3F_7$; Mn=2770, 8 g/dm^3: 5 ml] containing sodium carbonate (1.0 mmol) was added an aqueous solution (2 ml) of calcium chloride (1.0 mmol). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. The mixture was centrifuged for 30 min, and the obtained product was washed repeatedly (three times) with water. Finally, the white product was dried under vacuum at 50 °C to constant weight (isolated yield: 90 mg). The expected product thus obtained was subsequently characterized as R_F-$(ACA)_n$-R_F/$CaCO_3$ composites by the use of elementary analyses for fluorine atoms (found: 1.44%; theoretical: 5.41%), FT-IR ν/cm^{-1}: 1,240 (CF_2)], thermogravimetric analyses (TGA), dynamic light scattering methods (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The modified PMMA film was prepared by casting the 1,2-dichloroethane solution (10 ml) of PMMA (0.95 g) and the 1,2-dichlroethane solution (10 ml) containing R_F-$(ACA)_x$-$R_F/CaCO_3$ composites (50 mg) on glass plates. The solvent was evaporated at room temperature, and the film formed peeled off and dried at 50 °C for 24 h under vacuum to afford the modified PMMA film (film thickness 194 μm). The contact angles for dodecane of both the surface and the reverse sides of this film was measured at room temperature by the use of the goniometer-type contact angle measurements.

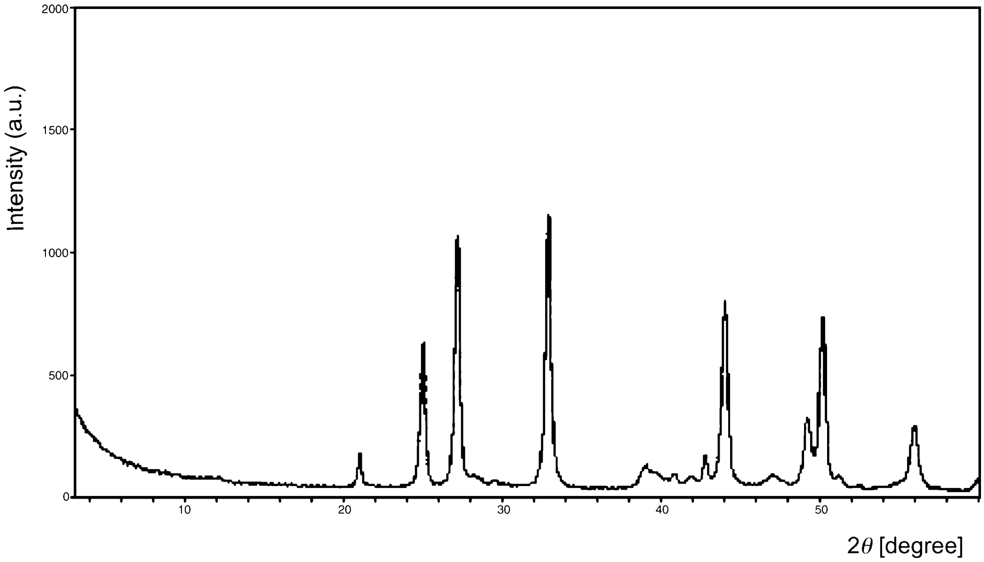


Fig. 8 X-ray diffraction of R_F-$(MES)_n$-$R_F/CaCO_3$ nanocomposite

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