

Preparation and Characterization of Core-Shell Nanoparticles Containing Poly(chlorotrifluoroethylene-co-ethylvinylether) as Core

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Received 20 December 2010; accepted 26 January 2011

DOI 10.1002/app.34262

Published online 10 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Core shell latex particles with a glassy core and a low T_g polymeric shell are usually preferred. More so, the glassy core happens to be a fluoropolymer with a shell polymer that helps in processability. We describe here the preparation and characterization of core shell nanoparticles consisting of poly(chlorotrifluoroethylene-co-ethylvinylether) as core encapsulated in poly(styrene-acrylate) copolymer shell using seeded emulsion polymerization method under kinetically controlled monomer starved conditions. Properties of the emulsion using surfactants (fluoro/conventional) and surfactant free conditions were investigated. Average size (100 nm), spherical shape and core-shell morphology of the latex particles was confirmed by dynamic light scattering

and transmission electron microscopy. Absence of C—F and C—Cl peaks in X-ray photoelectron spectroscopy proves that cores are completely covered. Polymerization in the presence of fluorocarbon surfactant was found to give optimum features like narrow size distribution, good shell deposition and no traces of agglomeration. Films of core shell latex particles exhibited improved transparency and enhanced water contact angles thus making them suitable for applications in various fields including coatings. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1807–1814, 2011

Key words: core-shell nanoparticles; chlorotrifluoroethylene; seeded emulsion polymerization; wettability

INTRODUCTION

Fluorine containing polymers have attracted increasing interest mainly because of their unique properties like heat stability, low moisture absorbance, chemical or weather resistance and low surface energy.^{1–3} They have wide application in paints, coatings, aerospace, optics, microelectronics^{4–6} and also as explosive binders in defense applications. However, because of their poor solubility, compatibility and inadequate adhesion to substrates need to be suitably modified. Several attempts for modification were done either by copolymerization with fluoro/nonfluoro monomer or surface modification via surface polymerization, grafting, sputtering, and plasma treatments.^{7–9} These methods are associated with a limitation of destroying the C—F bond that requires either highly reactive chemicals or high energy input. Therefore, alternative approaches of modification wherein preparation of core shell morphologies consisting of fluoropolymer as a core, sur-

rounded by a conventional polymeric shell have been explored in the recent past. Advantage of this approach is not only to improve the wettability and compatibility of the fluoropolymer but also help retain its original structure and properties yielding in a stable and homogeneous modification at molecular level.

Core shell particles are usually synthesized by a two-stage emulsion polymerization with synthesis of core latex particles in the first stage, which is used as seed in the second stage polymerization of shell monomers. Several polytetrafluoroethylene (PTFE)-polyacrylate core-shell morphologies were studied using pre-emulsified PTFE powder^{10,11} or a commercial PTFE emulsion^{12,13} either using a combination of emulsifiers or an emulsifier free method¹⁴ wherein micro-molecular level mixing of the two immiscible polymers was emphasized resulting in enhanced wettability characteristics. A convenient synthesis of fluoroalkyl acrylates and conventional acrylate copolymer latexes by miniemulsion polymerization¹⁵ resulted in core-shell morphology, on employing low doses of surfactants in a joint heterophase situation. A perfect degree of dispersion of the PTFE-polystyrene core-shell nanospheres could be obtained when the shell polymer flows, fills the voids forming a continuous polymer matrix resulting in efficient

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Contract grant sponsor: Terminal Ballistics Research Laboratory, Chandigarh, India.

PTFE based additives.¹⁶ Novel classes of such highly specific additives were made using PTFE core and crosslinked polybutadiene, crosslinked polystyrene, or polymethylmethacrylate shell.¹⁷ PTFE-PA core-shell nanospheres with low glass transition temperatures of the shell forming materials could permit the preparation of soft matrix nanostructured films.¹⁸ However, most of the fluoropolymer core shell composite particles reported so far used PTFE as core and to our knowledge there have been very few reports on preparation of core shell particles using other fluoropolymers as core.

In our laboratory, we have been working on development of fluoroelastomers based on copolymers of CTFE. We were keen on exploring the possibility of preparing core shell nanoparticles using CTFE based fluoropolymer as core and a conventional polymeric shell with a lower glass transition temperature, such that, annealing at an intermediate temperature or evaporation of water from the latex might allow the film formation. This film would have uniformly distributed CTFE copolymer particles in a shell polymer that imparts improved wettability and compatibility characteristics to the fluoropolymer. Therefore, in the present study, poly(chlorotrifluoroethylene-*co*-ethylvinylether) [Poly(CTFE-*co*-EVE)] latex nanoparticles were synthesized and employed as seed in the emulsion polymerization of acrylic monomers that will yield in Poly(CTFE-*co*-EVE)/poly(styrene-acrylate) copolymer (PSA) core shell nanoparticles. Effect of different experimental conditions like presence of a fluorocarbon surfactant (FS), mixture of conventional ionic and nonionic surfactants (MS) and surfactant free (SF) atmosphere were explored. A correlation of their physicochemical characteristics to their appearance, thermal stability and wettability of the composite nanoparticles were assessed.

EXPERIMENTAL

Materials

Butyl acrylate (BA), styrene (St) and acrylic acid (AA) were purchased from Aldrich chemicals. These compounds were distilled under reduced pressure and stored at 5°C. Sodium dodecyl sulfate (SDS) and polyoxyethylene-octylphenylether (TritonX100), sodium persulfate, sodium metabisulfite, borax and ferrous sulfate were purchased from SD fine chemicals, India and were used as received. Ammonium persulfate (APS), ethylvinylether (EVE) and heptadecafluoro octane sulfonic acid potassium salt (FS), a fluorosurfactant purchased from Fluka were used without further purification. Chlorotrifluoroethylene (CTFE) was a gift from Fluoroorganics division, Indian Institute of Chemical Technology, Hyderabad.

Synthesis of poly(CTFE-*co*-EVE) core nanoparticles

In a 500 mL Hastelloy autoclave equipped with a pressure gauge, mechanical stirrer, safety rupture disc and feedlines, a mixture of sodium persulfate (0.123 g, 0.0517 m moles), ferrous sulfate heptahydrate (0.018 g), borax (1 g), sodium dodecyl sulfate (2 g) and deionized water (150 mL) was charged. The reactor was then cooled to -60°C with dry ice/acetone bath, evacuated and flushed with nitrogen to exclude air from the reactor. The contents of the reaction vessel were subjected twice to freeze thaw cycles with evacuation and flushing of nitrogen and finally left under vacuum at -60°C. To the frozen contents, ethyl vinyl ether (18.62 g, 0.258 mol) and sodium metabisulfite (0.098 g, 0.0517 m moles, dissolved in 5 mL water) were transferred using canula. Later, CTFE (30 g, 0.258 mol) was condensed in to the reactor by gravimetrically monitoring the weight difference of CTFE cylinder. The reactor was then warmed to 37°C and stirred at 900 rpm. Pressure at the beginning of the reaction was found to be 100 psi which gradually dropped to 30 psi over 8 h as the reaction progressed. Polymerization was stopped when the pressure remained constant by venting out the unreacted CTFE in a hood and the copolymer emulsion was collected. A yield of 30 g of polymer was obtained as determined by solid content of the emulsion. Part of the polymer was lyophilized and purified by extensive washing with water for chemical characterization. Thus isolated polymer was further purified by dissolving in ether and precipitation by addition of hexane. The copolymer thus synthesized had a number average molecular weight (M_n) of 188,824, weight average molecular weight (M_w) of 385,168 and M_w/M_n of 2.03.

¹H-NMR (CDCl₃) δ: 4.3–4.7 (m, CH₂—CH(O)—CF₂), 3.6–3.9 (m, CH₂O), 2.2–3.2 (m, CH₂CF₂), 1.0–1.3 (m, CH₃) ppm.

¹⁹F NMR (CDCl₃) δ: -123 to -109 (m, CF₂CFCl) ppm.

FTIR: 1262 cm⁻¹: C—F stretch in CF₂; 1149 cm⁻¹: C—O stretch in C—O—Et; 759 cm⁻¹: C—Cl stretch.

Elemental analysis: Calculated: C = 38.19%, H = 4.24%; Found: C = 38.17%, H = 4.37%.

Synthesis of core-shell poly(CTFE-*co*-EVE)/PSA nanospheres

Preparation of core-shell Poly(CTFE-*co*-EVE)/PSA was carried out by seeded emulsion polymerization using Poly(CTFE-*co*-EVE) as seed particles following a semicontinuous process under kinetically controlled monomer starved conditions. All polymerizations were carried out in a 250-mL four-necked flask equipped with reflux condenser, mechanical stirrer, dropping funnel, and inlet for nitrogen gas, at 75°C.

TABLE I
Recipe for Synthesis of Core-Shell Poly (CTFE-co-EVE)-PSA Nanospheres

Samples	PCTFE-co-EVE (g)	St (g)	BA (g)	AA (g)	SDS (g)	Triton X100 (g)	FS (g)	APS (g)	DI water (g)	% of monomer conversion	% of yield
PSA	–	19.5	24.5	1	0.6	0.6	–	0.3	100	85.47	85.27
CS (MS)	3	19.5	24.5	1	0.6	0.6	–	0.3	100	72.47	75.74
CS (FS)	3	19.5	24.5	1	–	–	1.2	0.3	100	69.12	72.21
CS (SF)	3	19.5	24.5	1	–	–	–	0.3	100	66.38	69.83

Appropriate amount of Poly(CTFE-co-EVE) latex was introduced into the reactor flask containing 100 mL of deionized water with 1.2% surfactant or surfactant free at room temperature. The mixture was constantly stirred at 300 rpm and purged with nitrogen gas; nitrogen gas was fluxed continuously during entire polymerization and then heated to 75°C. A mixture of comonomers St, BA, and AA (44, 54, 2 wt %) and an appropriate amount of APS aqueous solution (0.5 wt %) were simultaneously dropped into the flask over a period of 2 h to maintain monomer starved conditions in the reactor. After the addition is complete, reaction mixture was heated further to 78°C and left for another 2 h. The latex obtained was purified from unreacted monomers and surfactants by repeated dialysis. In all polymerizations the amount of core latex, comonomer ratio and their corresponding weight percent was kept constant with changes in the type of surfactants used, FS (heptadeca fluorooctane sulfonic acid potassium salt) or MS (Triton-x-100 and SDS) and SF(surfactant free) conditions. The samples were labeled as Poly(CTFE-co-EVE), PSA and three core shell composite particles as CS(FS), CS(MS), and CS(SF). An emulsion polymerization reaction using pure shell monomers (PSA) mixture was also prepared for comparison. The details of recipe for reactions are given in Table I.

Characterization

The solid content of latex dispersion was determined gravimetrically. Conformation of presence of functional groups was done using Fourier transform infra red (FTIR) spectroscopy recorded on a Thermo Nicolet nexus 670 spectrometer. Transmission electron microscopy (TEM) pictures of the core shell nanoparticles were studied on a Philips Technai instrument. Diluted samples were stained with uranyl acetate and mounted on 400-mesh carbon coated copper grids and left to dry. Particle size and size distribution were obtained by dynamic light scattering (DLS) analysis performed at 25°C, with a Malvern Nano ZS at a fixed scattering angle of 90°, using a 10 mV He–Ne laser and PCS software for Windows (version 1.34, malvern, UK). Thermogravimetric analysis (TGA) was performed with a TGA Q500 Universal TA instrument at a heating rate of

10°C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis of the samples was performed on a DSC Q 100 Universal instrument. Samples were run in aluminum pans and scanned at a heating rate of 10°C/min under N₂ atmosphere. Static contact angles were measured on a contact angle goniometer (Kruss GMBH German G10MK2) by the sessile drop method at 25°C. Deionized water was dropped, with a micro-syringe on the surface of the latex films. Average of the angles obtained at more than 10 different locations on each sample surface was reported. Size exclusion chromatography was carried out at 30°C with Shimadzu Prominence apparatus equipped with Polymer Laboratories column (PL Gel 1110-6550) and an evaporative light scattering detector (PL ELS2100). Tetrahydrofuran was used as solvent (0.5 mL/min) and a series of narrow molecular weight polystyrenes as standards. Elemental analysis was done on Microcube analyzer of Elementar. NMR spectras were recorded on Avance 300 model of Varian in CDCl₃ solvent using TMS as internal reference.

RESULTS AND DISCUSSION

Synthesis of fluoropolymer core

Copolymers of CTFE with alkyl vinyl ethers like *n*-Butyl and 2-ethylhexylvinyl ethers using emulsion polymerization method were invented way back in 1957.¹⁹ Curable terpolymers of CTFE with cyclohexyl, ethyl, and hydroxyethyl vinyl ethers were later reported by solution polymerization for coatings applications.^{20–23} Solution copolymerization of CTFE with EVE was explored in solvents such as ethylacetate²⁴ and acetonitrile²⁵ using solvent soluble peroxy initiators.

Poly(CTFE-co-EVE) emulsions for the present work were prepared adopting a procedure reported¹⁹ for CTFE copolymerization with butylvinylether and the scheme is shown in Figure 1. Preliminary emulsion polymerization experiments showed that presence of buffer was essential because the vinyl ethers are known to be sensitive to acidic pH. Since simple thermal initiation using sodium persulphate provided polymer of low molecular weight, redox initiation at ambient temperature was

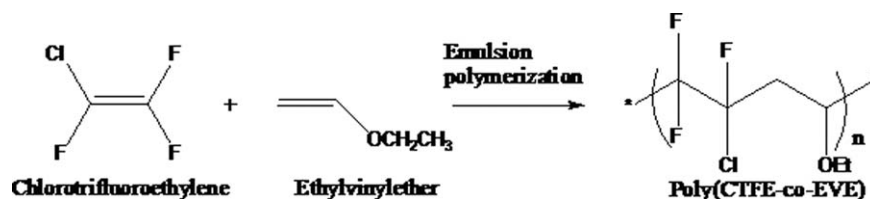


Figure 1 Synthesis of Poly (CTFE-co-EVE).

investigated at different monomer to initiator ratios and the details are shown in Table II. The experiment with redox initiation using 0.1 mol % initiator has yielded a copolymer with higher molecular weight in comparison to others.

$^1\text{H-NMR}$ of the copolymer synthesized is shown in Figure 2(b). It agrees well with reported values for this polymer.²⁵ The peaks appear to be broad and unresolved. This is attributed to presence of a range of diastereomers in the structure of the copolymer due to the presence of enantiomeric centers on alternating carbons.²⁵ The peaks represent an average of resonance for all the conformations possible for the structure. Figure 2(a) shows the ^{19}F spectrum of the polymer which also agrees well with reported spectrum.²⁵ Copolymer structure was also confirmed by FTIR which showed absorptions due to both monomers and is discussed in greater detail in the later part of this section. EVE and CTFE happen to be a donor-acceptor pair and are known to result in alternate copolymers and it was indeed found to be the case in the present synthesis also. Elemental analysis values for carbon and hydrogen of the polymer corresponded well with the theoretically calculated values for 1 : 1M ratio of the monomers.

Synthesis of core shell polymers

The Poly(CTFE-co-EVE) core shell emulsions were prepared by taking appropriate amount of Poly(CTFE-co-EVE) latex into deionized water and dropwise addition of calculated amounts of acrylic comonomer mixtures at 75°C over 2 h using APS as an initiator. Both the monomer mixture and the initiator solution were added simultaneously at the rate of 0.4 mL min^{-1} such that monomer starved conditions are maintained constantly until complete

addition is done. The presence of surfactants was found to yield monodispersed latex particles, but agglomeration of the latex was noticed in surfactant free conditions.

Structural properties

Figure 3 shows the FTIR spectra of Poly(CTFE-co-EVE) (core), PA (Shell) and Poly (CTFE-co-EVE)/PA composite nanoparticles. The FTIR spectrum of core displays the characteristic absorption peaks at 2971 and 2929 cm^{-1} (C–H stretching modes), 1458 and 1376 cm^{-1} (C–H bending modes), 1216 , 1122 , and 1063 cm^{-1} (C–O–C stretching modes), the CF groups stretching, CF_2 groups (C–F asymmetric stretching mode) and (C–F symmetric stretching mode) in the region between 1222 and 1130 cm^{-1} and at lower wave numbers 759 cm^{-1} (C–Cl stretching mode).^{20,26,27} When the core particles are covered with shell, the FTIR spectrum of composite particles show the peaks originated from PSA in addition to the characteristic peaks of core particles. The peak at 3435 cm^{-1} (O–H stretching mode) and 1730 cm^{-1} (–C=O stretching mode) are observed in the spectrum of Poly(CTFE-co-EVE)/PSA particles for all three core shell samples [CS (FS, MS, and SF)] indicating the presence of both the polymers used.

Size and morphology of the coreshell particles

An increase in the diameters of the core shell particles was noticed for all the samples and the low PDI values confirm that there is no occurrence of secondary nucleation giving a clear evidence of monomodal distribution as shown in Figure 4. The CS (FS) and CS (MS) have shown narrow

TABLE II
Effect of Initiator and Reaction Conditions on Molecular Weight of the Core Fluoropolymer

Run	Initiator	Temperature	Molecular weight		
			M_n	M_w	M_w/M_n
1	Potassium persulphate (0.2 mol %)	80°C	47,894	125,359	2.6
2	Redox (0.5 mol %)	35°C	115,905	221,806	1.9
3	Redox (0.1 mol %)	35°C	188,824	385,168	2.0

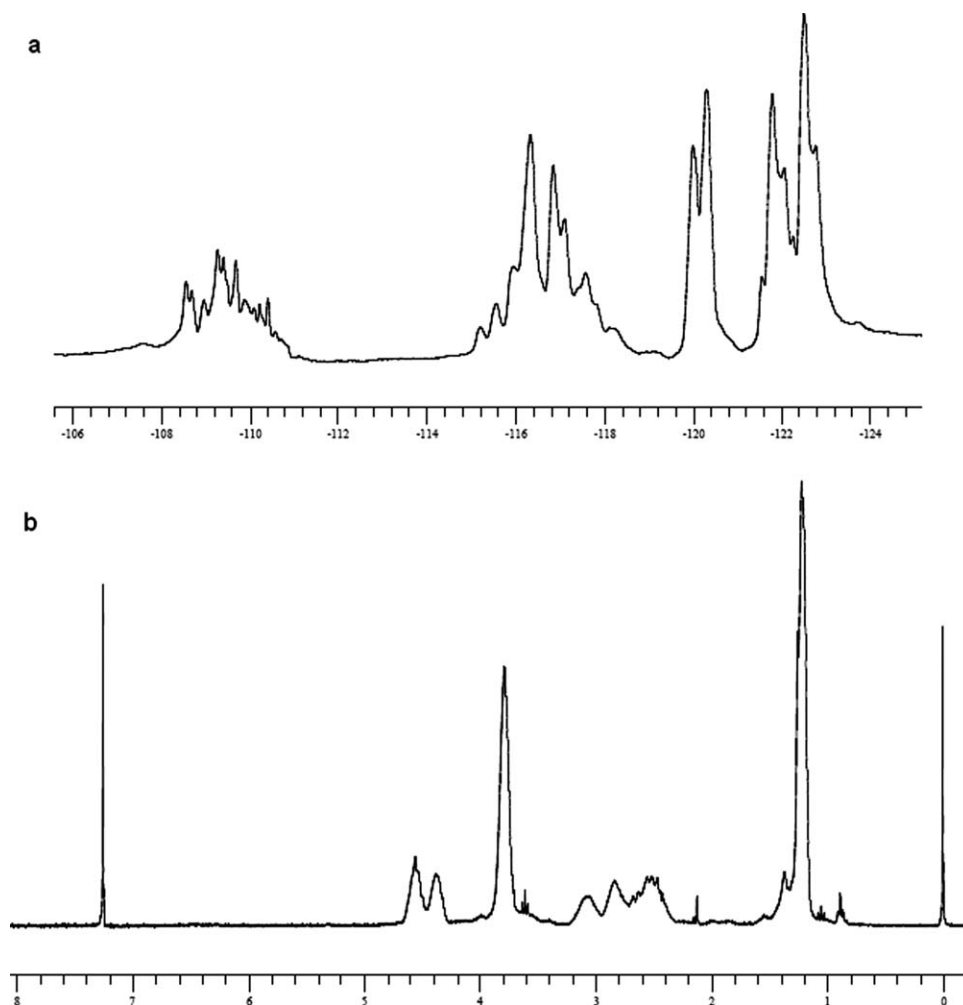


Figure 2 NMR spectra of core, Poly (CTFE-co-EVE). (a) ^{19}F and (b) ^1H .

distribution of size in comparison to CS(SF) which resulted in a broader distribution according to DLS. This observation agrees well with the agglomeration of the core shell latex observed during the synthesis as mentioned in the earlier section. Both CS (FS) and CS (MS) were subjected to TEM for finding the morphology. Careful staining of the particles with 2% uranyl acetate helped in differentiating the light region as the cores and the dark regions as the shell material. TEM picture for CS (FS) given in Figure 5 indicates a core shell formation which is quite distinct with a good shell deposition whereas such a clarity was not noticed in case of CS (MS) whose TEM picture is not given. Thus, fluorosurfactant was found to be more effective in getting the required core-shell morphology rather than the mixture of commonly used surfactants. Core shell formation for CS (FS) was further confirmed by studying the surface properties using X-ray photoelectron spectroscopy (XPS).

The XPS spectra's of the pure Poly(CTFE-co-EVE) and core shell of Poly(CTFE-co-EVE)/PSA are shown

in Figure 6. The characteristic signals for carbon (C_{1s} at 284.5 eV), oxygen (O_{1s} at 531 and 532 eV), fluorine (F_{1s} at 687 eV) and chlorine (Cl_{2p} at 200 eV)¹⁰ were detected for the Poly(CTFE-co-EVE). Whereas, core shell particles CS(FS) showed signals for carbon (C_{1s} at 284.5 eV) and oxygen (O_{1s} at 531 and 532 eV) with no indication of signals coming from fluorine and chlorine, thus confirming complete encapsulation of fluoropolymer core by shell polymer.

Thermal properties

The DSC curves of all the samples are shown in Figure 7. Poly (CTFE-co-EVE), the core fluoropolymer shows a glass transition (T_g) at 29°C and a specific endothermic peak at 85°C. It could be the melting peak corresponding to a first order phase transition of the copolymer. Shell polymer (PSA) shows a glass transition at 19°C which is known for such styrene acrylate copolymers. We had recorded the thermal behavior of all the core shell samples and found a single T_g falling in between the core

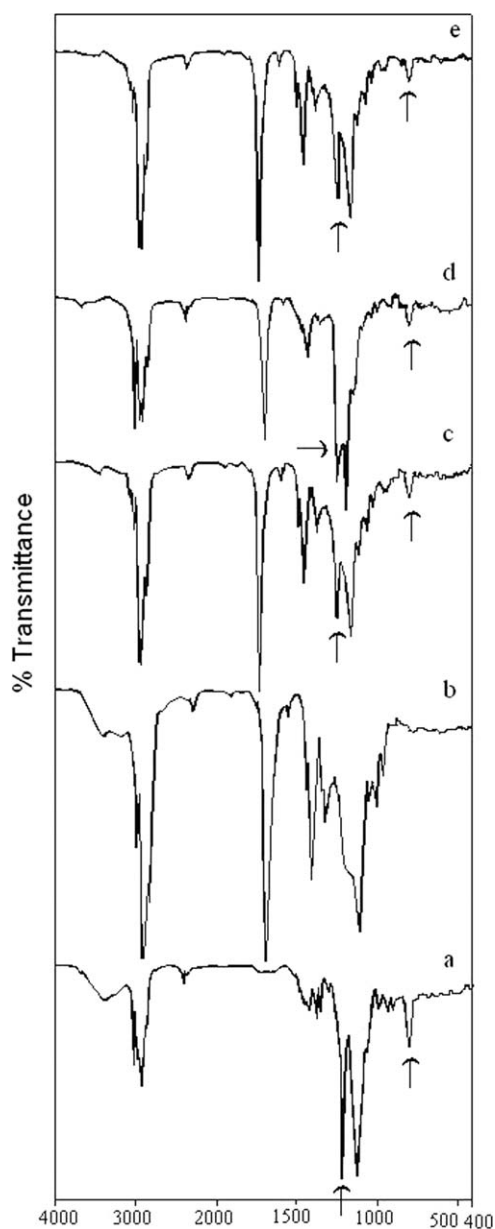


Figure 3 FTIR spectra of (a) Poly(CTFE-co-EVE), (b) PSA, (c) CS(FS), (d) CS(MS), and (e) CS(SF).

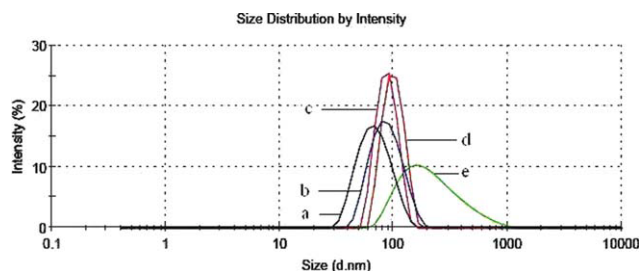


Figure 4 DLS spectra of (a) PSA, (b) Poly(CTFE-co-EVE), (c) CS (MS), (d) CS (FS), and (e) CS (SF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

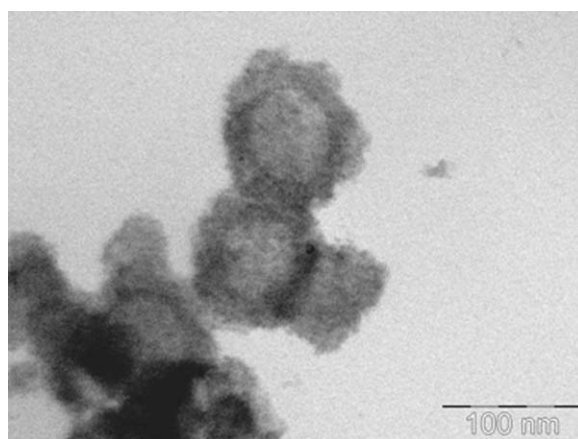


Figure 5 Transmission electron micrographs of CS (FS).

and shell polymers for all the samples and another transition beyond 100°C which could be the shifted peak corresponding to the first order transition of the fluoropolymeric core. This behavior clearly indicates the presence of both the polymers whose glass transitions are shifted on formation of composite particles due to the molecular level mixing of polymers but with no definite chemical interaction.²⁸

All the samples were subjected to TGA analysis, to investigate their thermal stabilities in comparison to their individual polymer components. The individual core and shell polymers start degrading at higher temperatures of 392 and 382°C, respectively, while degradation of all the core shell structures occurred between the two polymers as seen in Figure 8. Thermal stabilities of core shell nanoparticles were found to be comparable and have shown no profound effect of variation in the experimental conditions

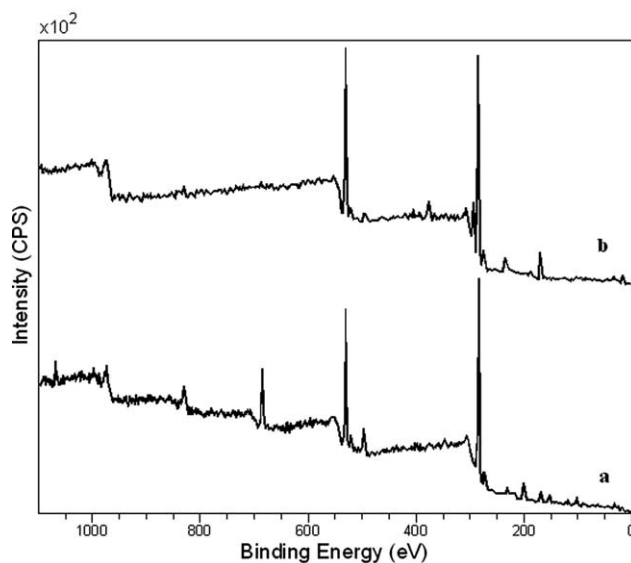


Figure 6 X-ray photoelectron spectra of (a) Poly (CTFE-co-EVE) and (b) CS (FS).

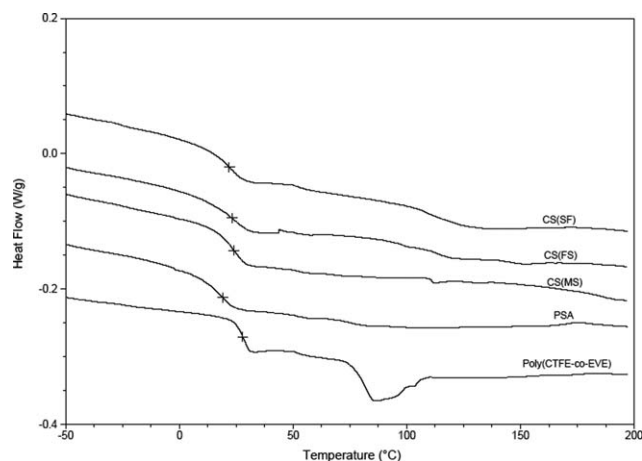


Figure 7 DSC of core shell nanoparticles.

like SF, FS or MS. A single degradation peak was noticed for all samples indicating an overlapping of both the components because of nearby values.

Appearance and wettability

All the samples are having good film forming ability but a remarkable improvement in transparency has been noticed on core shell formation as shown in Figure 9. A physical blend of core and shell polymers is slightly hazy and colored which is also shown for comparison.²⁹ Water contact angles are a measure of surface hydrophilicity/hydrophobicity and give an insight into the free energy of the surface. Fluoropolymers are known for their hydrophobicity with a reported contact angle value of 88° for CTFE homopolymer¹¹ and the copolymer of the Poly(CTFE-co-EVE) was measured to be 86°. It should be noted that a surface with a contact angle of 90° or higher is considered a “nonwetting” surface and below that is considered “wetting.” All core shell samples CS (MS), CS (FS) and CS (SF)

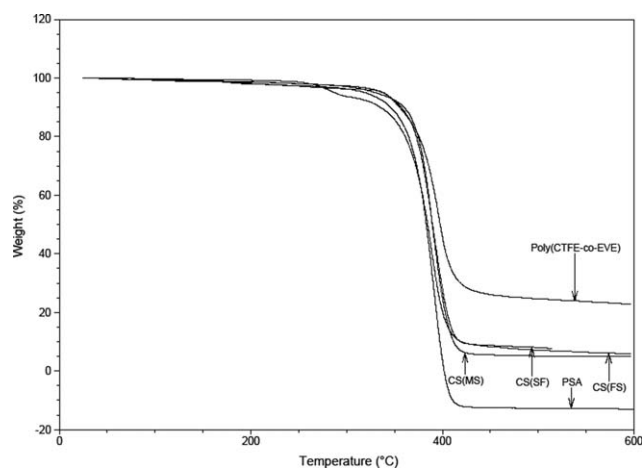


Figure 8 TGA of core shell nanoparticles.

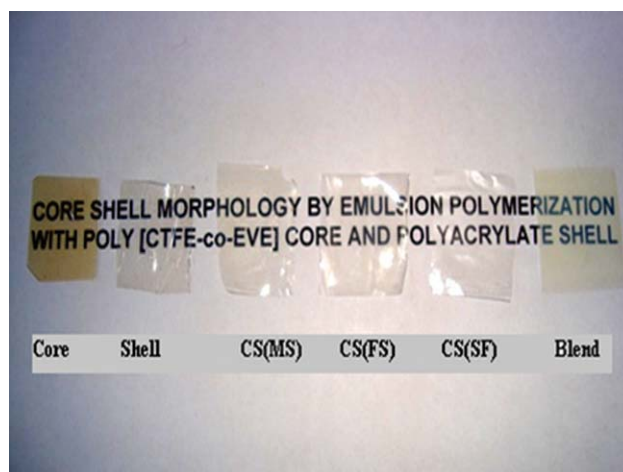


Figure 9 Films of core, shell, core-shell nanoparticles, and blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

have shown reduction in their water contact angles and are given in Table III. Formation of the PSA shell around the fluorocopolymer core has reduced the water contact angle by 24°, thus making it a good wetting surface from an almost nonwetting one. Increase in wettability (hydrophilicity) can be understood based on the fact that there are strong interactions between water and the hydrophilic groups such as —OH, C—O and C—O—C groups originated from polyacrylate shell enwrapped on the Poly(CTFE-co-EVE) surface.

CONCLUSION

It was shown that core-shell nanospheres with a fluorinated core of Poly(CTFE-co-EVE) could be successfully synthesized by a two stage emulsion polymerization. Kinetically controlled emulsion polymerization with continuous maintenance of monomer starved conditions has lead to an effective encapsulation of the core. Formation of composite particles was noticed from FTIR. Core-shell morphology, size, and monodispersity were examined and confirmed by TEM, XPS, and DLS. Core-shell particles exhibited a single degradation pattern in TGA and also a single T_g that falls in between the

TABLE III
Water Contact Angles of Core and Core-Shell Nanoparticles

Samples	Contact angle
Poly(CTFE-co-EVE)	86°
PSA	62°
CS (MS)	63°
CS (FS)	62°
CS (SF)	62°

individual core and shell polymers indicating the molecular level mixing of both the polymers with an indicative first order transition of the core polymer shifted to higher temperature. There was considerable effect of presence of surfactants; both the FS and MS have yielded in a fine core shell emulsion according to DLS, but morphologically FS was superior giving a distinguished shell deposition than MS. However, the absence of the surfactant (SF) resulted in agglomeration. The core shell particle formation gave transparency to the films and improved wetting property, thus imparting compatibility to the fluorocore with other materials facilitating its application in several suitable areas like paints and coatings.

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