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Polymer chemistry. Part 3. Gamma-ray induced encapsulation of titanium dioxide using fluorinated alkenes

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Abstract

Encapsulation of titanium dioxide with fluorinated monomers occurs readily by gamma-ray initiated selective polymerisation onto the surface of titanium dioxide suspended in FC-1,1,3 Studies of electron microscopy and XPS established uniform and complete encapsulation

Introduction

In the previous part of this series [1], we described a novel method for encapsulation of titanium dioxide and other inorganic solids, from solution in FC-1,1,3 using a variety of vinylic monomers, including fluoroacrylates. During this surprising process, gamma-ray induced polymerisation occurs almost exclusively at the surface of titanium dioxide, with remarkably little polymer in solution, or on the sides of the containing vessel. Here, we now confirm that various fluorinated alkenes may be used in the analogous process, giving highly novel materials in which particulate titanium dioxide is encapsulated wholly and uniformly in fluorinated polymers.

Results and discussion

We have modified the methodology described previously, to suit the use of volatile fluorinated alkenes. In this case the fluorinated alkene was condensed into a tube containing a suspension of titanium dioxide in FC-1,1,3 which was then sealed, before irradiation with gamma rays. During irradiation, the tube was rotated on a vertical axis to give good agitation.

In each experiment, little or no fluorinated alkene was recovered and only small amounts of polymer were obtained by evaporation of the

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TABLE 1

Results of γ-ray-induced encapsulation of titanium dioxide (TiO_2) with fluorinated alkenes

TiO_2[a] (g)	Monomers[b] (g)	Rad.dose (Mrad)	Products[c] S/P (g/g)	Remarks[d]
*RUT-W	TFE			XPS (–):
2.0	0.96	1.863	2.85/0.01	graphite
0.5	0.28	1.611	0.64/ –	on the surface
0.5	–	1.611	0.44/ –	
*RUT-W	VDF			
2.0	0.95	1.863	2.90/0.02	
*RUT-W	CTFE			
2.0	1.77	1.863	2.95/0.54	
ANA-W	TFE			XPS (–):
1.65	0.44	1.823	1.93/0.04	$Ti^{4+} > Ti^{2+}$
ANA-W	VDF			
2.33	0.53	1.823	2.74/0.04	
ANA-W	CTFE			
2.30	0.43	1.823	2.23/0.33	
RUT	TFE			
2.44	0.60	1.594	2.87/0.03	XPS (–)
RUT	VDF			
2.32	0.58	1.594	2.72/0.02	XPS (+)
RUT	CTFE			
2.23	0.55	1.594	2.17/0.40	
RUT	MAA/TFE			
2.48	0.03/0.58	1.623	2.94/0.02	XPS (+)
RUT	MAA/VDF			
2.49	0.03/0.56	1.623	2.89/0.03	
RUT	MAA/CTFE			
2.58	0.03/0.53	1.623	2.47/0.57	
–	TFE			
–	0.88	1.376	– /0.86	polymer standards
–	VDF			
–	0.58	1.376	– /0.56	
–	CTFE			
–	1.08	1.376	– /0.84	
RUT-520	TFE			
1.00	0.84	1.633	1.84/ –	XPS (–)
0.25	–	1.633	0.25/ –	
RUT-520	MAA/TFE			
1.07	0.012/0.83	1.633	1.83/ –	XPS (+)
0.32	0.004/ –	1.633	0.26/ –	

TABLE 1 (continued)

TiO_2[a] (g)	Monomers[b] (g)	Rad.dose (Mrad)	Products[c] S/P (g/g)	Remarks[d]
RUT-520-W	TFE			
0.12	0.08	1.633	0.20/ –	
ANA-520	TFE			
1.00	0.91	1.867	1.86/ –	
0.25	–	1.867	0.25/ –	
ANA-520	MAA/TFE			
1.00	0.012/0.88	1.867	1.83/ –	
0.34	0.004/ –	1.867	0.34/ –	
RUT-1050	TFE			
1.00	0.41	2.083	1.41/ –	
RUT-1050-W	TFE			
1.00	0.40	2.083	1.40/ –	
0.75	–	2.083	0.75/ –	
TC-90	MAA/VDF/HFP			
5.00	0.05/1.38/0.97	1.173	6.64/0.17	
2.00	0.02/1.18/0.76	1.173	3.45/0.18	

[a] RUT = rutile; ANA = anatase, w = washed beforehand with methacrylic acid solution (3% on weight of pigment) in Freon 113 and then with more solvent; 520 = after annealing in oxygen atmosphere at ~520 °C (14 h); 1050 = annealing at ~920 °C (16 h), followed by 4 h at 1050 °C; TC-90 = rutile obtained via chloride process, Tioxide supplier.

[b] MAA = methacrylic acid; TFE = tetrafluoroethylene; VDF = vinylidene fluoride; CTFE = chlorotrifluoroethylene; HFP = hexafluoropropene.

[c] S = solid pigment isolated by filtration; P = polymer obtained from filtrate by evaporation of solvent under vacuum.

[d] XPS (+) = where good X-ray photoelectron spectrum was obtained; XPS (–) = where poor or no coating was detected either by EM or XPS.

*Dried at 190 °C (oven), discolouration of products observed.

recovered solvent. The exception was chlorotrifluoroethylene, where a significant amount of polymerisation occurred in the solution.

The titanium dioxide was examined by electron microscopy (EM) and the surface by XPS, and it was established that relatively uniform films were formed and that no titanium dioxide was exposed on the surface. The range of materials is illustrated in Table 1 and these even include a co-polymer between hexafluoropropene and vinylidene fluoride.

In the examples shown in Table 1, incorporation of some methylmethacrylic acid (MAA) was used, but in some cases this was not necessary, *e.g.* with vinylidene fluoride. Thus it appears that, if a sufficiently polar molecule is involved, MAA is not required to initiate the process. Previously, the processes that we described employed significant proportions of MAA to promote the process, but we have now established that, even with non-polar molecules like tetrafluorethylene, only a small

TABLE 2

Results of γ-ray-induced encapsulations of titanium dioxide pigment with 2,2,2-trifluoroethyl methacrylate (TEMA) and methacrylic acid (MAA)

Pigment[a]	Coating system	Solvent[b] (ml)	Products (E/R)[c]
(g)	(g/g)	Rad dose (Mrad)	(g/g)
TR-92	MAA/TEMA	400	
200	5/25	0 945	223/3
TC-90	MAA/TEMA	1500	
500	15/60	1 440	566/7
TC-90	MAA/TEMA	1500	
500	5/100	1 623	582/11
TC-90	MAA	1250	
500	100	1 390	600/ –
–	MAA[d]	20	powder
–	1 0	1 680	1 0
–	TEMA[d]	20	glassy
–	1 0	1 680	– /1 0
–	MAA/TEMA[d]	20	powder/grease
–	0 36/0 66	1 680	1 25/0 14
–	MAA/TEMA[d]	20	powder/grease
–	0 2/1 0	0 910	0 6/0 2

[a] TR-92 = pigment obtained via sulphate route, TC-90 = pigment obtained via chloride route

[b] 1,1,2-trichlorotrifluoroethane

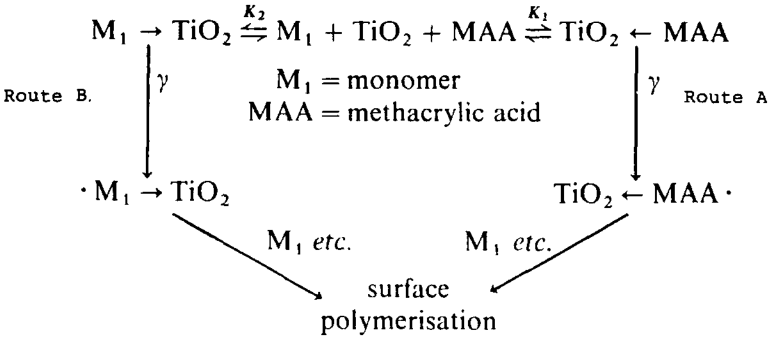
[c] E = encapsulated pigment or solid polymer obtained by filtration, R = residual polymer obtained from filtrate (solvent) by evaporation under vacuum

[d] Pre-treated with TC-90 and centrifuged (5 min, 1000 rpm) or filtered, preparation of polymer standards for comparison

amount (*ca.* 1 wt %) of MAA is required relative to the weight of pigment. Examples are given in Tables 1 and 2.

The mechanism of the process is intriguing, and we propose that shown in Scheme 1. Thus the process could occur by added MAA (Route A) or by direct interaction of the monomer with titanium dioxide (Route B). We have demonstrated that methylmethacrylate is *not* strongly adsorbed on titanium dioxide and, therefore, the equilibrium constants K_1 or K_2 are quite small, but obviously sufficient to allow the process to occur. We have argued previously [1] that preferential absorption of gamma-rays by titanium dioxide, rather than the organic components of the system, is the key to the process, hence promoting radical formation in close proximity to the surface. We have carried out further mechanistic probes and have established conclusively the following:-

(i) The process *does not* involve 'living polymerisation' because attempts to irradiate before exposure to alkene did not lead to encapsulation.



Scheme 1.

(ii) Preferential adsorption of the preformed polymer from solution *does not* occur because we were unable to adsorb significant amounts of polymer from solution, with or without gamma-ray irradiation.

(iii) Other methods of initiation, *e.g.* peroxides or ultraviolet light, gave solution polymerisation or polymers deposited on the walls of the vessel.

(iv) Ionic mechanisms seem unlikely because isobutene, which polymerises readily by the cationic process but not by a radical mechanism, was not polymerised in this process, see Table 3.

We can conclude, therefore, that the process is specific to gamma-rays and the mechamism is most probably that outlined in Scheme 1; MAA is essential in some cases but in relatively small proportions.

Thus we have described our route to some highly novel composite materials, which are clearly important to evaluate. We have demonstrated that the material coated with PTFE may be sintered, to form a disc with PTFE-like properties; and we have 'processed' the titanium dioxide coated with hexafluoropropene–vinylidine fluorinated elastomer, to effect cross-linking. Furthermore, we have carried out contact-angle

TABLE 3

Attempted γ-ray induced encapsulation of rutile titanium dioxide (RUT) with isobutene (1.611 M rad rad. dose)

RUT (g)	MAA/isobutene (g/g)	Solvent (ml)	Products (S/L)[a] (g/g)
2.00	– /0.54	20	1.98/0.35
2.00	0.02/0.54	20	1.98/ –
–	– /0.53	20	– /0.05

[a] S = solid material obtained by filtration; L = liquid obtained by evaporation of solvent under vacuum.

TABLE 4

Contact angle measurements[a]

Contact angle (deg)	Characterisation of material[b]
152	PTEMA/TC-90
130	PMMA/TR-92
126	PMMA/TR-92 (from emulsion polymerisation, material supplied by Tioxide Co)
98	PVAc/TC-90
180	PTEMA/TC-90 + PTEMA (G 48-1), rest polymer 481), obtained from solvent, not wettable
ap 70	PMMA (Aldrich), comparison measurement
ap 10	plain glass microscope slide

[a] All samples from encapsulated or polymeric materials had been prepared as suspensions or solutions in ethyl acetate, painted with brush on a glass microscope slide and dried under vacuum. All measurements were carried out with a drop of water ~2 μl at intervals less than 1 min after application. A Rene-Hart NRL Contact Angle Goniometer 100-00 was used for the measurements.

[b] Acronyms – see previous Tables and [1].

measurements, see Table 4, and it is quite clear from the results that the surface properties of these materials are very significantly influenced by the coating.

The process of encapsulation may be scaled up, see Table 2, with remarkable levels of selective encapsulation *vs.* soluble polymers and in each case, uniform coatings were obtained. Comparatively small amounts of polymer were obtained from solution. Furthermore, in separate experiments, this polymer was not adsorbed from solution onto the surface of titanium dioxide.

Experimental

Chemicals used

Unless otherwise indicated (see Tables), titanium dioxide (TiO_2) was used as supplied (suppliers indicated); 99.9% rutile (RUT) or anatase (ANA), Aldrich Chemical Co. supplier, and pigments TR-92 and TC-90, obtained via the sulphate or chloride routes respectively (Tioxide UK, Ltd.).

Tetrafluoroethene (TFE) was purchased from PCR Co., vinylidene fluoride (VDF), chlorotrifluoroethene (CTFE) and 2,2,2-trifluoroethyl methacrylate (TEMA) form Fluorochem Ltd., and methacrylic acid (MAA) from Aldrich Co.

1,1,2-Trichlorotrifluoroethane (CFC, 113) was obtained from ICI plc as Arklone P solvent and used as purchased, except those experiments with annealed rutile and anatase (see Table 1) in which the solvent was dried with molecular sieves and distilled before use.

Procedure

The majority of experiments were performed using sealed Pyrex Carius tubes (*ca.* 80 cm^3) by the procedure described earlier [1]. Powdered TiO_2 (usually 1–5 g) was slurried in the reaction tube with CFC, 113 (20 ml), containing in some cases MAA. When the amount of TiO_2 was less than 1 g, 10 ml tubes and 4 ml of CFC, 113 were used. Gaseous alkenes were condensed via vacuum transfer to this mixture, and the contents of the tubes were degassed in three freeze–thaw cycles. The tubes (usually a set of three) containing frozen reactants were sealed under vacuum and then placed in a Carius tube holder fastened to the rotor of the slow running motor in a vertical position. The tubes were then irradiated at 24 cm distance with a ^{60}Co γ-source (*ca.* 550 Ci). The total radiation dose was calculated using the Fricke dosimeter technique. Solid products were recovered from the tubes and isolated by filtration, followed by drying under vacuum (oil vacuum pump) for several hours either at room temperature or in a boiling water bath (especially in the case of preparation of polymer standards, which followed the same procedure excluding the presence of TiO_2). The filtrate was worked up by removal of solvent under vacuum to recover soluble polymers from solutions in CFC, 113.

The bulk experiments (see Table 2) were carried out using a polyethene bottle (2 l) with a screw cap. Solid pigment was suspended in the reaction vessel with CFC, 113 containing MAA and a stream of nitrogen (for de-oxygenation of the reaction mixture) was bubbled through the mixture for several minutes. After addition of TEMA, the reaction vessel was closed, fastened in the holder described above, and exposed to irradiation while being slowly rotated in a vertical axis. The preparations of polymer standards referred to in Table 2 were carried out by the above procedure using Carius tubes and solutions of monomers in CFC, 113 which were pre-treated with pigment to absorb inhibitors before γ-induced polymerisations. Encapsulated material was isolated by filtration and dried under vacuum in a round-bottom flask (placed in a boiling water bath) connected via a cooled trap to retain residual CFC. Remaining soluble polymer fractions were obtained from filtrates when CFC, 113 had been distilled off.

XPS spectra

X-ray photoelectron spectra were acquired on a Kratos ES300 surface analysis instrument. Mg K_α radiation was used as the excitation source with electron detection in the fixed retarding ratio (22:1) analyzer mode. The gold $4f_{7/2}$ level at 83.8 eV had a full width at half maximum (FWHM) of 1.2 eV. The powder samples were mounted onto a probe tip using

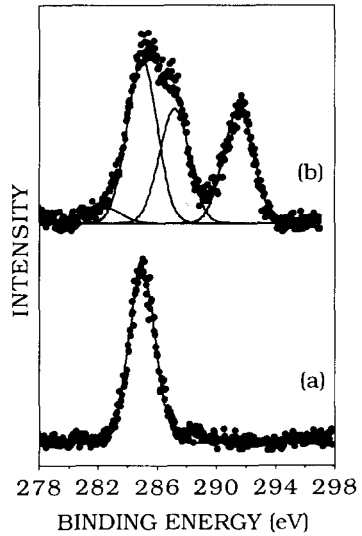


Fig. 1. Peak fit of C(1s) XP spectra for (a) TiO_2 starting material; (b) $CF_2{=}CH_2/TiO_2$ following gamma-ray irradiation. (●): raw data, and (——): individual gaussians.

double-sided adhesive tape. XPS measurements were taken with an electron take-off angle of 30° from the surface normal. No evidence was obtained for radiation damage to the samples during the typical time scale involved in these experiments. Data accumulation and component peak analysis were performed with an IBM PC computer, using linear background subtraction and gaussian fits. For any particular experiment, all the different C(1s) $K\alpha_{1,2}$ environments were assigned a constant FWHM. Additional $K\alpha_{3,4}$ satellites (with a different fixed FWHM) were needed for the $-\underline{C}F_2$ groups. The relative intensities of the peaks within any particular C(1s) envelope were fitted in accordance with the theoretical values expected from the monomer structures. All binding energies are referenced to the hydrocarbon component at 285.0 eV. No differential charging was observed, since there was always one F(1s) feature with no asymmetry in its peak shape.

Figure 1 shows the C(1s) XP spectra of TiO_2 particles as received, and following exposure of $CF_2{=}CH_2/TiO_2$ solution to gamma-rays. The C(1s) environments were assigned according to the literature values for the bulk polymers [2, 3]: $-CF_2\underline{C}H_2-$ ($K\alpha_{1,2}$) at 286.8 eV, $-\underline{C}F_2CH_2-$ ($K\alpha_{1,2}$) at 291.3 eV, and $-\underline{C}F_2CH_2-$ ($K\alpha_{3,4}$) at 282.3 eV; (it should be noted that some hydrocarbon contamination was also present at 285.0 eV). With these films, an attenuated XP signal from the TiO_2 substrate was still evident. If uniform encapsulation is assumed, a rough esimate can be made of the film thickness by considering the extent of attenuation in the $Ti(2p_{3/2})$ XP intensity; a 95% decrease in substrate signal correlates to 45 Å ($\approx 3\lambda$) of polymeric coating [4] (λ, the inelastic mean free path of Ti($2p_{3/2}$) photoelectrons through an organic overlayer is ≈15 Å) [5].

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