Final Report

Supercritical Fluid Infusion of Iron Additives in Polymeric Matrices

Presented to

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May 1999

1. Objective

Preparation of iron nanophases within polymeric matrices via supercritical fluid infusion of iron precursors followed by thermal reduction.

2. Experimental

2.1-Materials

All polyimide films (BTDA/ODA, BTDA/APB, PMDA/4,4′ ODA, PMDA/APB) were provided by NASA Langley Research Center (Hampton, VA) and used as received. They were all transparent, flexible and had a yellow color. Poly(etheretherketone), PEEK, film was obtained from McMASTER-CARR supply company (Dayton, NJ.). This film was transparent, colorless, flexible and had a smooth surface on one side and much rougher surface on the other film side. Poly(methylmethacrylate), PMMA, was obtained from Aldrich Chemical Company (Milwaukee, WI.) as a powder and then pressed to make a film. The film was transparent, colorless, and brittle. Polysulfone (PS) was obtained from Amoco (Napierville, IL.) as a pellet and then was pressed to make a film. The film was colorless and brittle.

The additives ferroceneacetonitrile (black color), cyclooctatetraeneiron tricarbonyl (dark red), triiron dodecacarbonyl (dark green), diiron nonacarbonyl (yellow) and iron pentacarbonyl (yellow liquid) were obtained from Aldrich Chemical Company (Milwaukee, WI.) and were used as received.

2.2- Supercritical Fluid Infusion and Cure Procedure

All supercritical fluid infusion (SFI) experiments were performed using an Applied Separations (Allentown, PA.) supercritical fluid system (Spe-ed SFE). In each experiment the film and the additive were placed together in a 10 ml stainless steel supercritical extraction vessel (Keystone Scientific, Bellefonte, PA.). All films had a dimension of 5×1 cm. and the dimensions remained constant after infusion and cure. The additive was introduced to the vessel containing the polymer film on a weight of additive/weight of film basis. CO_2 at the selected pressure was added and the vessel was heated to the desired temperature for a given time to achieve supercritical conditions. Upon completion of the experiment, the vessel was decompressed to ambient pressure for about 1-2 minutes. After removing the film from the vessel the edges of the film were

clamped between two glass plates and heated in an oven at a selected time and temperature with compressed air circulation of 30 standard cubic feet per hour (SCFH). All infusion experiments were performed with Air Product and Chemicals Inc. (Allentown, PA.) CO_2 and CHF_3 each pressurized with 2000 psi helium. The following parameters were used for all infusion and cure processes:

- **Fluid:** SC-CO_2, SC-CHF_3
- **Infusion Pressure:** 2200 psi
- **Infusion Temperature:** 100°C
- **Infusion Time:** 120 min.
- **%Weight of Additive/Polymer:** 20
- **Cure temperature:** 200°C
- **Cure Time:** 20 min.
- **Cure Air Flow Rate:** 30 Standard cubic feet per hour (SCFH)

2.3- Measurements

X-ray photoelectron spectra were obtained via a Perkin-Elmer Phi Model 5400 ESCA system. A magnesium anode (Ka=1253.6 eV) operating at 400W was used. Cited binding energies were relative to an assumed aromatic carbon signal of 284.6 eV. The samples were attached to mounts by double stick tape. Transmission electron micrographs were taken with a Philips Model 420 transmission electron microscope. Samples prepared for TEM were embedded in Polyscientific's ultra-low viscosity medium and cured for 12 hours at 60°C. Using a Reichert-Jung ultra-microtome with a microstar diamond knife, cross sections of the samples between 500 and 1000 angstroms were obtained. Iron mass analysis was obtained by Galbraith Laboratories, Inc.(Knoxville, TN). Glass transition temperature (T_g) was obtained by NASA Langely Research Center (Hampton, VA.).

3. Results and Discussions

3.1- Polymer Infusion with Supercritical Fluids

To determine if supercritical CO_2 could infuse into the polymer, strips of polymer film were individually subjected to 2200 psi CO_2 at 110°C for 120 minutes. There was no apparent change in the color or the texture of any of the films and only a slight change in

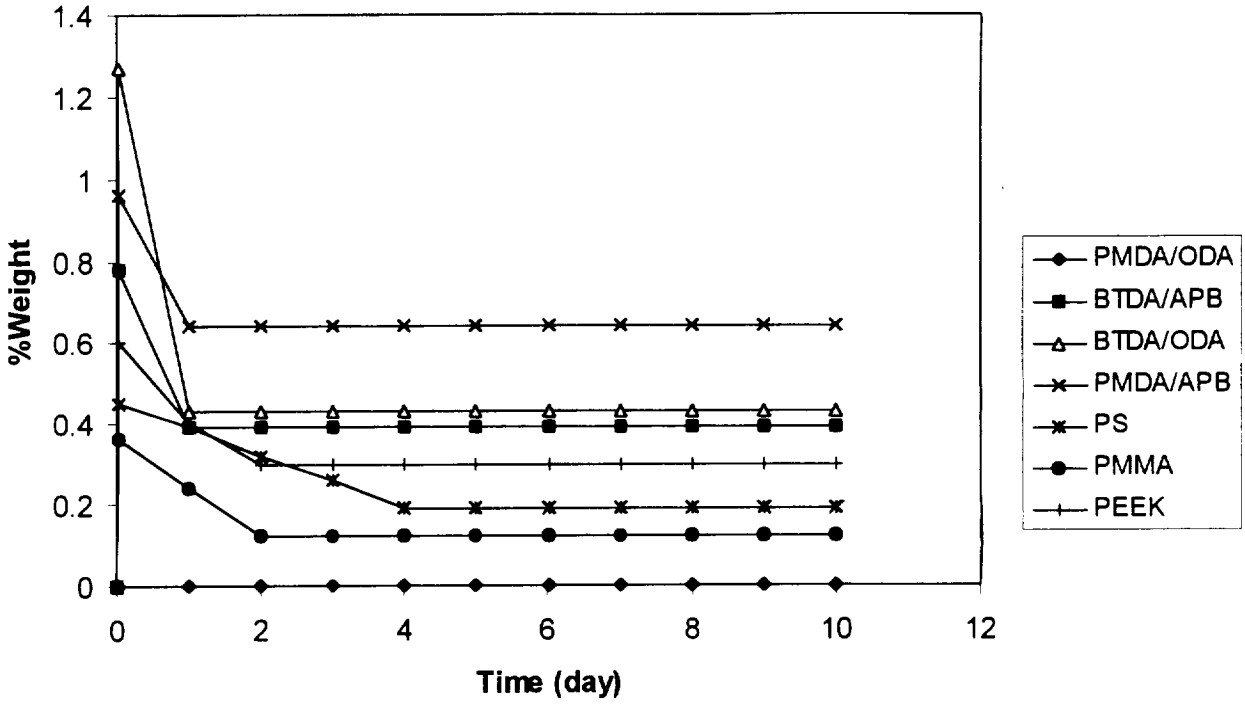


Figure 1- Mass change for polymer films upon treatment with supercritical CO_2 and then decompression

(Infusion conditions: 100°C/2200 psi/120 min.)

film mass was observed (Figure 1) after CO_2 decompression. The weight of the film was monitored each day for ten days. The weight gained by each sample 30 minutes after the infusion process was plotted as "zero day". All of the films except PMDA/ODA gained weight and retained a portion of the weight even after ten days. PMDA/APB showed the greatest permanent increase in weight. Thus, supercritical CO_2 may penetrate the polymers, but we concluded that little CO_2 remained in the films when the pressure was reduced to ambient pressure and temperature. The same study was performed using CHF_3 as a supercritical fluid and again, there was no apparent change in the color or the texture of any of the films and only a slight change in mass was observed for each film except PMDA/ODA (Figure 2) after decompression. In a few cases there was a considerably greater gain in weight with CHF_3 than CO_2. BTDA/ODA exhibited over 2.5% weight gain, while PS and PMMA were just above 1.5% weight gain. Although PMMA lost all its gained weight in a few days, BTDA/ODA exhibited approximately 1.0% weight gain after 10 days.

3.2- Polymer Infusion with Additives and Supercritical Fluids

Incorporation of iron additives into polymer films via supercritical fluids may be dependent on both the infusion and curing conditions in addition to the nature of the additive. The study of the effect of different supercritical fluids (CO_2, CHF_3), different infusion parameters (%weight additive, temperature, pressure, time) at constant cure conditions and also, the effect of different cure parameters (temperature, time, airflow rate) at constant infusion conditions with four precursors has been performed.

Tannenbaum et al.[1] demonstrated the preparation of metal carbonyl solid solutions in polymers and the phase separation decomposition of the organometallic complex to form uniform metal or metal oxide dispersions of very small particle size. In this approach, organometallic complexes were dissolved in polymer solutions to form homogeneous mixtures. These solutions were then cast and the resulting films exposed to thermal, photolytic or electron beam energy. These treatments decomposed the organometallic complex to form fine uniform dispersions of metal or metal oxide particles in the polymer matrix. In this system $Fe(CO)_5$ was selected as the organometallic complex with the following polymers: bisphenol polycarbonate, polystyrene, polysulfone and polyvinylidene fluoride.

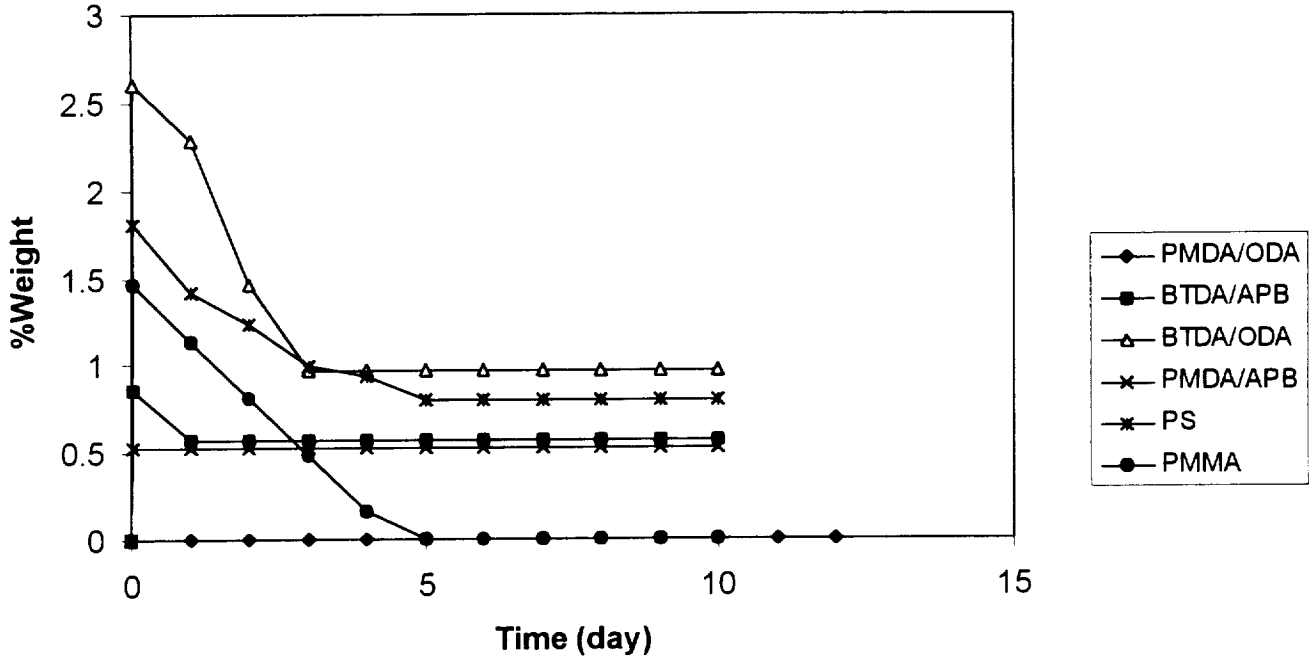


Figure 2- Mass change for polymer films upon treatment with supercritical CHF_3 and then decompression

(Infusion conditions: 100°C/2200 psi/120 min.)

Our first attempt involved the use of CO_2 and the infusion of 20% additive (ferroceneacetonitrile, cyclooctatetraeneiron tricarbonyl, triiron dodecacarbonyl and diiron nonacarbonyl) into four polyimides; while infusion temperature, pressure and time were held constant (100°C/2200 psi/120 min.). After the infusion and decompression process, the films were immediately cured at 200°C for 20 minutes in a flowing air stream (i.e. 30 standard cubic feet per hour (SCFH)). No changes in film color were observed but in most cases after the infusion and cure process some converted additive was deposited on the surface of the film. Occasionally some additive could be seen in the vessel.

Elemental surface atomic compositions from XPS for selected films are presented in Tables 1-4. For each sample we looked at two different spots on the same film side. The highest amount of iron (about 12 atomic percent) was obtained using BTDA/APB with triiron dodecacarbonyl. Also, the results of iron surface atomic concentrations from XPS using CHF_3 as a supercritical fluid under the above infusion and cure conditions are shown in the same Tables. In this case, the highest amount of surface iron (about 9.7 atomic percent) was obtained using BTDA/ODA with triiron dodecacarbonyl.

Since the highest concentrations of iron were observed using triiron dodecacarbonyl and CO_2, a view of the internal physical structure of three selected doped films (BTDA/ODA, BTDA/APB, PMDA/ODA) was obtained by transmission electron microscopy (TEM) of film cross sections. In all three cases, the TEM showed a continuous layer on the surface but there were no particles inside the bulk (Figures 3-5).The thickness of each layer on BTDA/ODA, BTDA/APB and PMDA/ODA was 10.5, 18.4 and 36.8 nm, respectively. TEM results on films infused with triiron dodecacarbonyl and CHF_3 under the same conditions also contained no bulk iron as reported by NASA Langley Research Center.

The thermal stability of these three films was obtained by performing thermal gravimetric analysis (TGA). PDT_{10} is a parameter corresponding to the temperature at which 10% weight loss occurs. The PDT_{10} for non-doped BTDA/ODA was 519°C. The observed PDT_{10} for infused BTDA/ODA with 20% triiron dodecacarbonyl and CO_2 was BTDA/ODA with 20% triiron dodecacarbonyl and CO_2 was 516°C. The PDT_{10} for non-doped BTDA/APB and PMDA/ODA were 515°C and 533°C, respectively, while for

Table 1- Iron Atomic Concentration (XPS) for Infused/Cured PI/ Films Containing Ferroceneacetonitrile

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Status	SCF= CO_2 (spot 1/ spot 2)	SCF= CHF_3 (spot 1/ spot 2)
BTDA/ODA	After cure	0.48/ 0.02	2.21/ 2.08
BTDA/APB (Film #1)	After cure	2.19/ 2.35	1.93/ 2.45
BTDA/APB (Film #2)	After cure	2.52/ 2.80	NA
PMDA/ODA	After cure	3.71/ 4.04	1.05/ 1.17
PMDA/APB	After cure	1.71/ 1.68	1.95/ 1.71

Table 2- Iron Atomic Concentration (XPS) for Infused/Cured PI/Films Containing Cyclooctatetraene Iron Tricarbonyl

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Status	SCF= CO_2 (spot 1/ spot 2)	SCF= CHF_3 (spot 1/ spot 2)
BTDA/ODA	After cure	0.00/ 0.00	1.05/ 1.84
BTDA/APB	After cure	0.47/ 0.68	1.54/ 1.96
PMDA/ODA	After cure	5.54/ 5.77	2.27/ 2.25
PMDA/APB	After cure	2.55/ 3.21	2.86/ 2.95

Table 3- Iron Atomic Concentration (XPS) for Infused/Cured PI/Films Containing Triiron Dodecacarbonyl

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Status	SCF= CO_2 (spot 1/ spot 2)	SCF= CHF_3 (spot 1/ spot 2)
BTDA/ODA	After cure	7.96/ 9.28	9.21/ 10.27
BTDA/APB (Film #1)	After cure	12.55/ 12.16	6.88/ 7.76
BTDA/APB (Film #2)	After cure	12.46/ 12.58	NA
PMDA/ODA	After cure	10.69/ 10.86	4.55/ 4.48
PMDA/APB	After cure	8.43/ 8.81	3.33/ 3.94

Table 4- Iron Atomic Concentration (XPS) for Infused/Cured PI/Films Containing Diiron Nonacarbonyl

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Status	SCF= CO_2 (spot 1/ spot 2)	SCF= CHF_3 (spot 1/ spot 2)
BTDA/ODA	After cure	2.84/ 3.00	7.19/ 7.61
BTDA/APB	After cure	6.60/ 6.72	5.06/ 7.48
PMDA/ODA	After cure	4.43/ 5.29	3.78/ 2.87
PMDA/APB	After cure	3.75/ 4.08	7.17/ 8.17

Figure 3- Transmission electron microscopy (TEM) of BTDA/ODA infused with $Fe_3(CO)_{12}$ and then cured

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)
(Magnification: 187,000x)

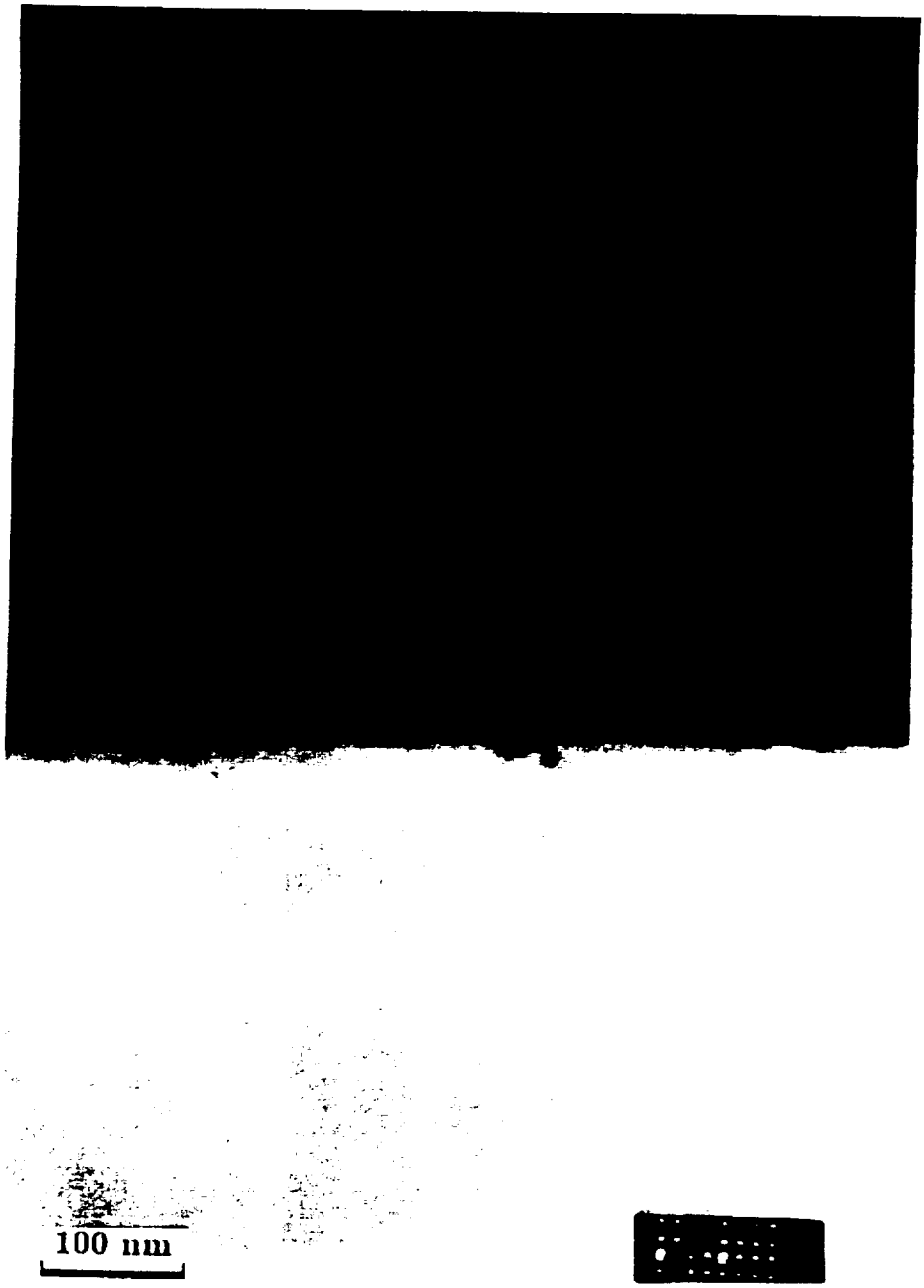


Figure 4- Transmission electron microscopy (TEM) of BTDA/APB infused with $Fe_3(CO)_{12}$ and then cured

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)
(Magnification: 187,000x)

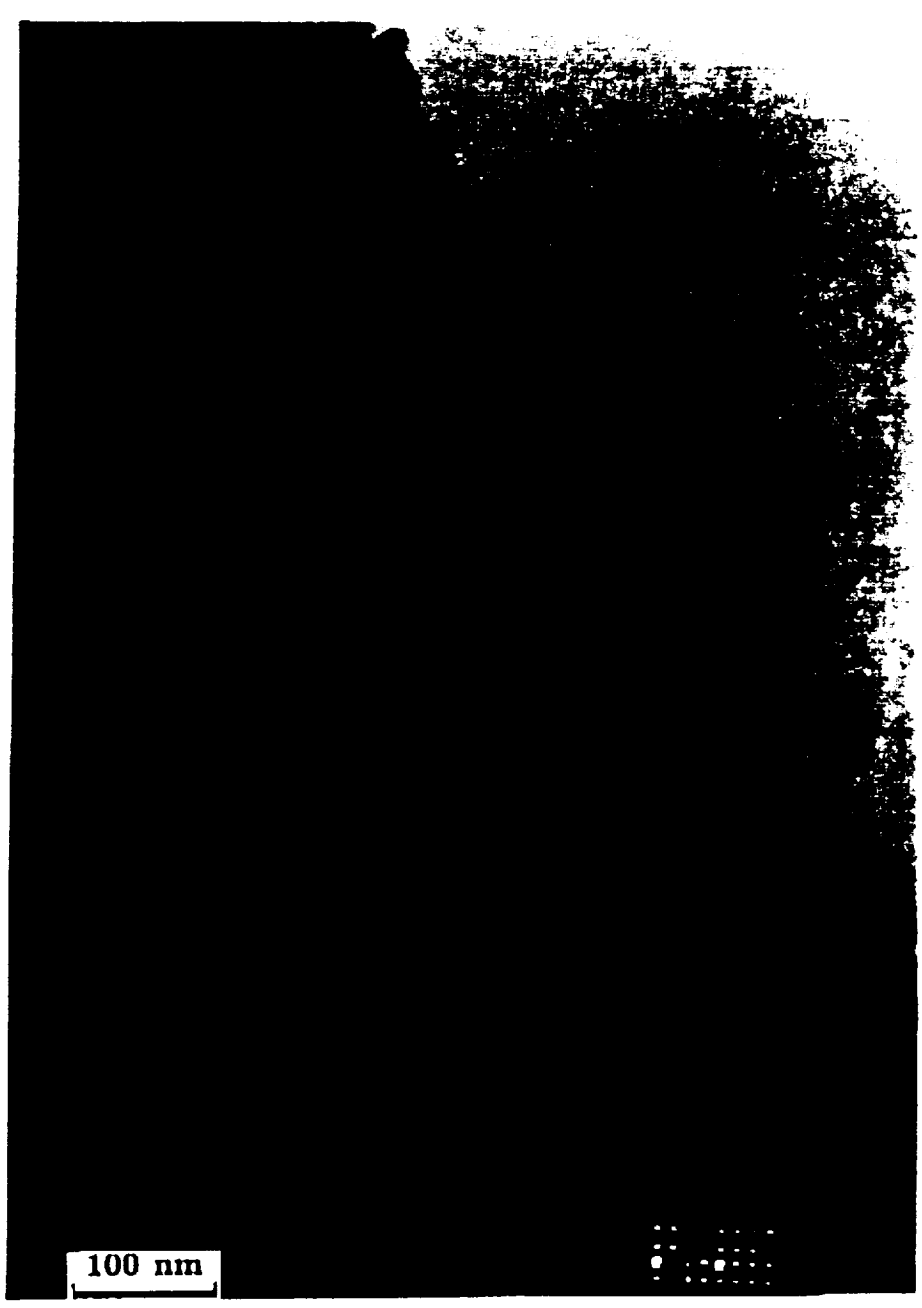
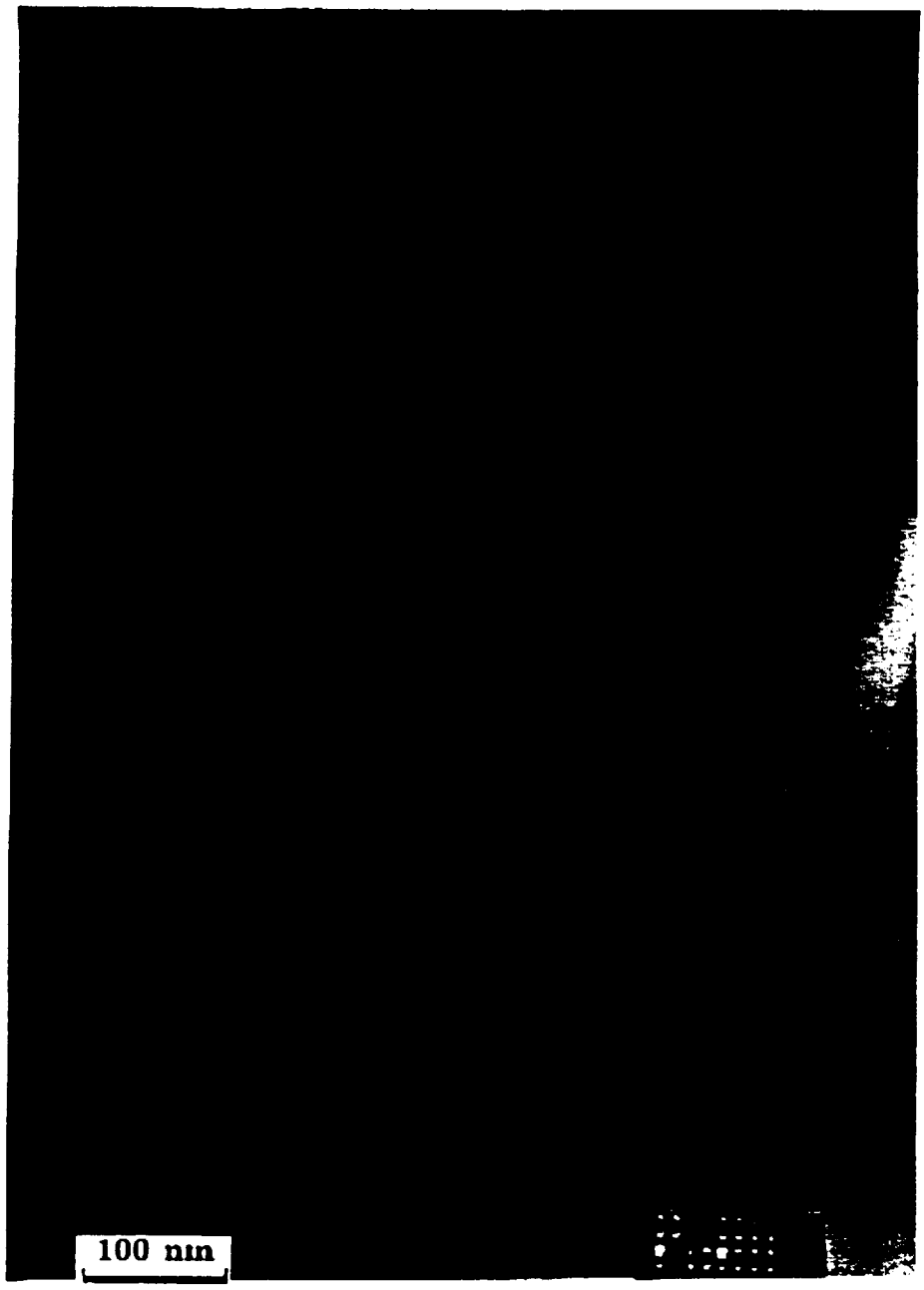


Figure 5- Transmission electron microscopy (TEM) of PMDA/ODA infused with $Fe_3(CO)_{12}$ and then cured

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)
(Magnification: 187,000x)



infused BTDA/APB and PMDA/ODA PDT_{10} was 502°C and 529°C, respectively. The difference between the PDT_{10} for the original and infused BTDA/ODA and also PMDA/ODA was not significant which provided more evidence that there was no iron in the film. The difference between PDT_{10} for infused BTDA/APB versus the original film was a little bit higher which suggested incorporation of a very small amount of iron into the film.

Based upon these findings our efforts became focused on the film with the highest atomic iron concentration (i.e. BTDA/APB/ triiron dodecacarbonyl). The chemical state of the iron in this film as suggested by XPS was iron oxide (Fe_2O_3) (Figure 6). The surface of many of the iron-containing films seemed to be covered with converted/unconverted additive. We, therefore, decided to clean the surface prior to infusion and see if this process had any effect on formation of the continuous Fe_2O_3 layer. Consequently, methanol was sprayed on to the surface of the infused BTDA/APB/triiron dodecacarbonyl/film and then it was cured. The XPS analysis as stated earlier for the unwashed iron film was found to be 12.3% iron on the surface; while, for the infused, washed after infusion, and then cured film we found 11.3% iron (Table 5). A second washed film after infusion yielded 8.5% iron on the surface. The TEM profile of this sample showed some particles on some parts of the surface (Figure 7). Iron percent by weight for this film was only 0.032%, but TEM revealed that practically all the iron was on the surface.

Next methanol as a modifier for CO_2 was employed during the infusion process to determine whether we could improve penetration of iron into the film. In the first experiment, BTDA/ODA was used. The additive was ferroceneacetonitrile. The film, 20% additive, and 0.5 mL methanol were placed in the vessel together. The infusion and cure conditions were the same as previously mentioned. The results of XPS analysis are shown in Table 6. This study showed that using a modifier did not significantly change the iron atomic concentration on the surface. The film also did not change color which suggested there was no incorporation of iron into the film. Similar results were obtained with BTDA/APB.

In hopes of improving the amount of iron in the film bulk, the effect of temperature and time during the thermal cure treatment was considered. Up to now, the

Figure 6- Iron (Fe 2p) photoelectron spectrum

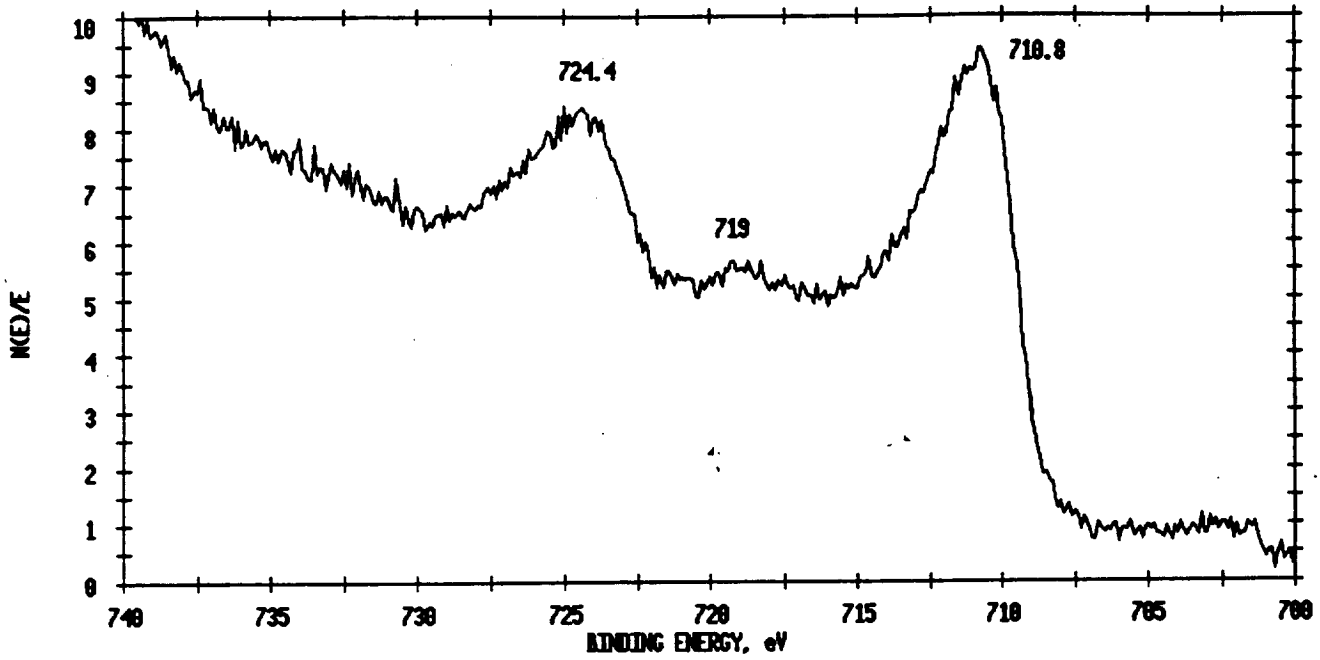


Table 5- Iron Atomic Concentration (XPS) for infused/ cured BTDA/APB Containing Triiron Dodecacarbonyl as a function of order of treatment

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Status	SCF= CO_2 (spot 1/ spot 2)	SCF= CHF_3 (spot 1/ spot 2)
After Cure	12.55/ 12.16	6.88/ 7.76
Inf./ Wash/ Cure	11.40/ 11.17	NA
After Cure	12.46/ 12.58	NA
Inf./ Wash/ Cure	8.48/ 8.57	NA

Figure 7- Transmission electron microscopy (TEM) of BTDA/APB infused with $Fe_3(CO)_{12}$, washedwith methanol and then cured

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)
(Magnification:187,500x)

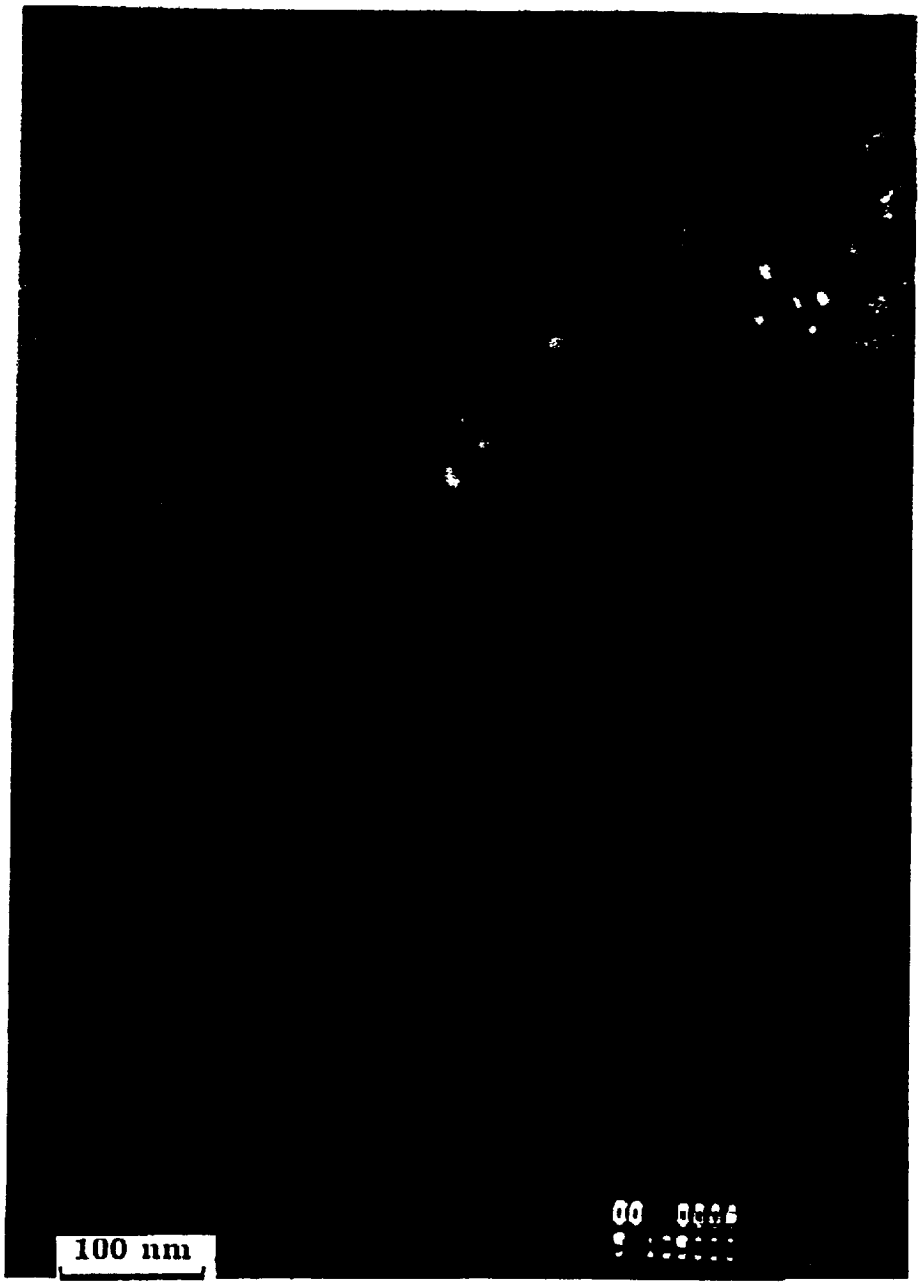


Table 6 - Iron Atomic Concentration (XPS) for Infused/Cured PI/ Films Containing Ferroceneacetonitrile

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Modifier	Status	SCF= CO_2 (spot 1/ spot 2)
BTDA/ODA	-	After cure	0.48/0.02
	Methanol	After cure	0.00/0.00
BTDA/APB	-	After cure	2.19/2.35
	Methanol	After cure	2.29/2.72

Table 7- Iron Atomic Concentration (XPS) for Infused (CO_2)/Cured BTDA/APB Films Containing Triiron Dodecacarbonyl for different cure conditions.

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

Cure conditions (°C/ min./ SCFH)	SCF= CO_2 (spot 1/ spot 2)
200/ 20/ 30	12.55/ 12.16
	12.46/ 12.58
300/ 20/ 30	1.30/ 1.15
300/ 60/ 30	0.26/ 0.31

usual cure conditions were 200°C/20 min./30 SCFH. To study the effect of cure temperature and time, two other experiments at constant infusion conditions (100°C/2200 psi/120 min.) were performed. In the first experiment, infused BTDA/APB/triiron dodecacarbonyl was cured at 300°C/20 min./30 SCFH. In the second experiment, infused BTDA/APB/triiron dodecacarbonyl was cured at 300°C/60 min./30 SCFH. There was a decrease in iron atomic concentration (Table 7) when the cure temperature increased from 200°C to 300°C at constant cure time and air flow rate (20 min/30 SCFH). Also, at 300°C/30 SCFH increasing the cure time from 20 to 60 minutes resulted in a decrease in surface iron atomic concentration.

We have also attempted the infusion of iron pentacarbonyl into BTDA/APB using CO_2 as a supercritical fluid. The infusion conditions were 100°C/2200 psi/120 min. and the cure conditions were 200°C/20 min/30 SCFH. No changes in color were observed in the film. The surface atomic iron concentration for this film via XPS analysis was approximately 3% (Table 8). Since it had been shown by other workers that $Fe(CO)_5$ undergoes decomposition in the presence of nitrogen nucleophiles[2], we attempted an infusion with triethylamine and $Fe(CO)_5$ together. To achieve this, two vessels were used. In the first vessel, there was just triethylamine and in the second vessel BTDA/APB and $Fe(CO)_5$ were placed. The infusion and cure conditions were the same as previously mentioned. Again no change in color of the film was observed. Table 9 shows some other infusion conditions, which were tried (at constant cure conditions) but none of them produced a change in film color. XPS analyses for these samples are not available.

For testing purposes a large infused film was needed. To achieve this study, a piece of BTDA/APB and 20% triiron dodecacrbonyl were placed together in a 500 mL stainless steel supercritical extraction vessel (Thar Design, Pittsburgh, PA.). The film had a dimension of 3″×3″ which remained constant after cure. The infusion conditions were 100°C/2200 psi/ 120 min. and CO_2 was used as the supercritical fluid . The film was cured at 200°C/20 min./30 SCFH. No changes in film color were observed after the infusion but some converted additive was deposited on the surface of the film and also some additive could be seen in the vessel. The results of iron surface atomic concentrations from XPS are summarized in Table 10. Since the sample was large we

Table 8- Iron Atomic Concentration (XPS) for Infused/ Cured BTDA/APB/$Fe(CO)_5$ Film

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Additive	Status	SCF= CO_2 (spot 1/ spot 2)
BTDA/APB	Diiron nonacarbonyl	After cure	2.45/2.91

Table 9- Supercritical infusion conditions of the BTDA/APB with 20wt.% $Fe(CO)_5$.

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

T(°C)	P(psi)	t (min)
100	2200	120
100	4000	120
150	2200	120
150	4000	120

Table 10- Iron Atomic Concentration (XPS) for Infused/ Cured BTDA/APB/$Fe_3(CO)_{12}$ Film Using 500 mL vessel

(Infusion Conditions: 100°C/ 2200 psi/ 120 min.)

(Cure Conditions: 200°C/ 20 min./ 30 SCFH)

Sample	Additive	Status	SCF= CO_2 (spot 1/ spot 2/ spot 3/ spot 4)
BTDA/APB	Triiron dodecacarbonyl	After cure	1.17/2.31/3.18/4.43

looked at four different spots randomly on the same film side. This result revealed that the amount of iron on the surface varied from 1.17 to 4.43%.

We have also attempted to infuse tris(hexafluoroacetylacetonato)iron(III) and tris(trifluoroacetylacetonato)iron(III) into BTDA/APB using CO_2 as a supercritical fluid. The infusion conditions were 100°C/2200 psi/120 min. and the cure conditions were 200°C/20 min./30 SCFH. No color changes were observed in the film. The XPS results are not available for these samples.

The study of the infusion of the iron additives into other polymers such as PEEK, PS, and PMMA is in progress.

Reference

1. Metal- Containing Polymeric Systems, Sheats, J. E., Carraher Jr., C. E., Pittman Jr., C. U., Ed. Plenum Press, NY, 1985.
2. Smith, T. W., Wychick, D., J. Phys. Chem., 84, 1621 (1980).