Modifier and Polymer Interactions in Metal-Modified Polyimide Composites

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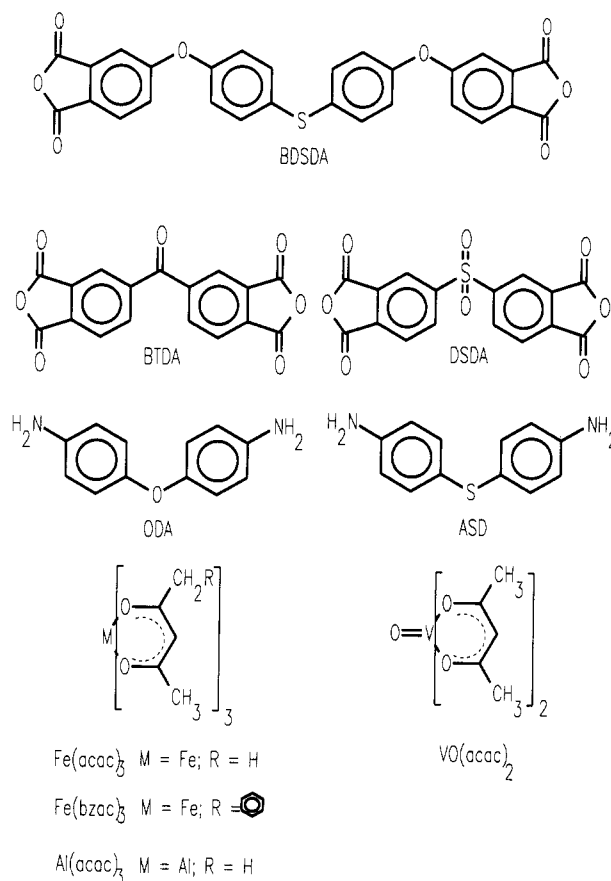Blacksburg, Virginia 24061-0212*

A sulfur-containing polyimide precursor has been modified by the homogeneous addition of tris(2,4-pentanedionato)iron(III) or tris(1-phenyl-2,4-pentanedionato)iron(III). The synthesis of the resulting free-standing film of iron-modified polyimide via thermal condensation is also described. It was observed that the presence of iron promoted the oxidation of the thioether moiety in the polyimide backbone as determined by X-ray photoelectron spectroscopy (XPS) and reflectance Fourier transform infrared spectroscopy (FT-IR). The effect of cure atmosphere on the oxidation of the sulfur, the thermal properties of the composite, and the distribution of iron oxide particles within the free-standing film are also examined.

Introduction

Polyimide films containing in situ generated metal/metal oxide particles have been studied by Taylor and co-workers[1–12] in an attempt to synthesize materials with unique combinations of properties. Specific modified polyimides have been shown to exhibit either enhanced electrical,[3] magnetic,[4] thermal, or adhesive[5,6] properties. For example, copper,[2,7] cobalt,[3,8] tin,[3] and iron[4] salts and/or complexes were converted to copper metal, Co_3O_4, SnO_2, and Fe_2O_3, respectively, during the poly(amide acid) curing process. The modified polyimide composites were produced in this manner without affecting the polyimide chemically. Since polyimides exhibit weak donor properties and the monomeric dianhydrides and diamines contained, in most cases, poorly donating ether and ketonic functionalities, no interaction of metal species and polyimide was ever apparent in these earlier studies.

Sulfur (thioether) containing monomers, however, have previously been implicated in metal–polyimide interaction. One of the dianhydrides used in several studies was 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA, Figure 1). Homogeneous dopants included

Figure 1. Monomers and modifiers used.

cobalt(II) chloride,[1,8–10] silver nitrate,[11,12] and bis(trifluoroacetylacetonato)copper(II).[7] The polyimide in these studies was synthesized from BDSDA and 4,4'-diaminodiphenyl ether (ODA, Figure 1). The presence of a metal additive in all three instances could be correlated via X-ray photoelectron spectroscopy with a distinct change in the chemistry of the thioether sulfur in the polyimide backbone. These previous studies presented differing interpretations to account for this chemically altered polyimide thioether.

In the study with copper,[7] it was believed that the copper was chelated to the thioether sulfur of the polyimide. The

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Metal-Modified Polyimide Composites

Chem. Mater., Vol. 6, No. 7, 1994 **991**

metal was hypothesized to be in a mixed oxidation state. TEMs from this study showed evidence of very few metal/metal oxide particles compared to similarly prepared non-sulfur-containing polyimides. Thus, it was hypothesized that the chelation of copper to the thioether moiety caused the metal to exist in a molecularly dispersed state.

In the cobalt study,[8] the sulfur was speculated to be catalytically oxidized by cobalt to sulfoxide and/or sulfone. The cobalt(II) chloride dopant, meanwhile, was converted to Co_3O_4. This interaction was only observed on the atmosphere (air) side of free-standing films. Coordination between the sulfur and cobalt was ruled out because it was believed that if coordination was the cause, then it should have been observed on both sides of the composite film. The state of the copper on the glass side was not reported in the copper/polyimide composite.[7] TEMs of the cobalt/polyimide composites were not included, so it was impossible to determine the exact particle distribution within the composite.

Both coordination and oxidation of the sulfur were considered in the silver/polyimide composite study.[12] FT-IR reflectance spectra failed to show any band attributable to either sulfone or sulfoxide. It was also observed that considerably more silver migrated to the atmosphere side of non-sulfur-containing polyimide composite compared to those containing sulfur. Possible silver coordination to sulfur was hypothesized as a reason for the reduced migration.

The dianhydride, BDSDA, has also been used in several other studies without metal modification. St. Clair and co-workers used this monomer in combination with either *p*-phenylenediamine or benzidine for the synthesis of polyimides with a high degree of crystallinity.[13] They also investigated this dianhydride in conjunction with several diamines as a possible source of optically transparent polyimide coatings.[14] Crivello et al. have studied BDSDA in the synthesis of high-temperature photoresist materials.[15] BDSDA was also one of the monomers examined by Takekoshi et al.,[16] in their study of thermal and physical properties of a series of polyimides. No chemical change in the thioether moiety was reported during processing in any of these studies.

St. Clair and co-workers have also used BDSDA to prepare a series of thermoplastic polyimides.[17-21] BDSDA and 1,3-bis(aminophenoxy)benzene were reacted to yield a polyimide adhesive that contained both phenylene oxide and sulfide groups.[17,18] This polymer exhibited the processibility of poly(phenylene oxides) and poly(phenylene sulfides) while maintaining the thermal stability and solvent resistance of polyimides. The lap shear strength of this adhesive was reported to be quite high compared to other polyimides.[18] Another thermoplastic polyimide, designated 422, has been synthesized using equimolar amounts of *m*-phenylenediamine and 4,4′-oxydianiline as

the diamine component.[19,20] This polyimide has found some application as a high-temperature adhesive for bonding titanium and Celion 6000/LARC-160 composite. Again, no chemical change in the thioether was reported in these studies.

The only study that made any note of a possible chemical change in the thioether was reported by Burks and St. Clair,[21] who examined the properties of polyimides synthesized from either BDSDA or its sulfone analogue (BDSO₂DA) and 3,3′-diaminodiphenyl sulfone (DDSO₂). Both nitrogen- and air-cured samples of BDSDA/DDSO₂ were investigated. They concluded that the thioether in both the fully air-cured and nitrogen-cured samples was oxidized to the sulfone moiety because they did not find any difference between the reflectance infrared spectra of these samples and that of BDSO₂DA/DDSO₂. Their interpretation of the spectra no doubt was very tenuous since a sulfone group from the amine monomer was present in all three samples prior to oxidation.

Our study builds upon the earlier studies with metal-doped BDSDA and ODA. Tris(2,4-pentanedionato)iron-(III) (Fe(acac)₃, Figure 1) was the main additive used in this study since it had been shown to be noninteractive with non-sulfur-containing polyimides.[4] Tris(1-phenyl-2,4-pentanedionato)iron(III) (Fe(bzac)₃) was used to examine the effect, if any, that the ligand had on the metal-sulfur interaction. Tris(2,4-pentanedionato)aluminum (Al(acac)₃) was also examined as a non-transition-metal additive comparable to Fe(acac)₃. The third modifier, bis-(2,4-pentanedionato) vanadyl oxide (VO(acac)₂), has been shown to be a catalyst for the oxidation of thioether sulfur.[22] The interaction between the thioether and the metal additive has potential application in the field of adhesives. The interaction between a sulfur-containing adhesive and a suitable metal substrate could enhance the interfacial strength by creating chemical bonds between the substrate and adhesive. It could also affect bond strength detrimentally by oxidative degradation of the adhesive along the interface creating a boundary layer which would weaken the interfacial strength. Thus, it is important to fully understand the iron–polyimide interaction.

Experimental Section

Materials. 4,4′-Bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA) was obtained from NASA Langley Research Center (Hampton, VA), recrystallized twice from 2-butanone, and vacuum dried overnight at 120 °C prior to use. The monomers and modifiers used are shown in Figure 1. Other dianhydrides which were examined include 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) which was obtained from Allco Chemical Corp. (Galena, KS) and was vacuum dried at 120 °C. 3,3′,4,4′-Diphenylsulfone tetracarboxylic acid dianhydride (DSDA) was obtained from Chriskev, Inc. (Leawood, KS) and vacuum dried at 110 °C. Zone-refined 4,4′-diaminodiphenyl ether (ODA) was obtained from Aldrich Chemical Co. (Madison, WI) and vacuum dried overnight at 70 °C before use. The other diamine examined was 4,4′-diaminodiphenyl sulfide (ASD) which was obtained from Mitsui Toatsu (Tokyo, Japan) and vacuum dried at 80 °C overnight. N,N-Dimethylacetamide (DMAc) was obtained from Aldrich Chemical Co. and was stored under nitrogen and over molecular sieves prior to use. The iron additives were tris(2,4-pentanedionato)iron(III) (Fe(acac)₃), obtained from Amspec, Inc. (Gloucester, NJ), and tris(1-phenyl-2,4-pentanedionato)iron(III) (Fe(bzac)₃), obtained from the National Institute of Standards and Testing (Washington, DC). Other additives include tris(2,4-pentanedionato)aluminum (Al-

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Table 1. Physical and Thermal Properties of BDSDA/ODA Composite Films

film	cure atm	color	flexibility	PDT air (°C)	PDT N$_2$ (°C)	T$_g$ (°C)
nonmod	air	yellow	creasible[a]	579	581	217
nonmod	nitrogen	yellow	creasible	613	594	217
Fe(acac)$_3$	air	red	bendable	442	553	261
Fe(acac)$_3$	nitrogen	red	creasible	464	560	248
Fe(bzac)$_3$	air	red	creasible	447	545	250

[a] Creasible refers to films that can be folded and creased twice in a perpendicular fashion without fracturing: bendable refers to films that can be folded but not creased without fracturing.

(acac)$_3$) and bis(2,4-pentanedionato)vanadium oxide (VO(acac)$_2$) both of which were obtained from Aldrich Chemical Co. All of the metal complexes were vacuum dried at 80 °C overnight prior to use.

Synthesis. Poly(amide acid) solutions were made by reacting equal molar amounts of diamine and dianhydride in DMAc (11% solids for BDSDA solutions and 18% solids for BTDA and DSDA solutions) under a nitrogen atmosphere. The monomers were allowed to react for at least 1 h in the stirred solution. After this period, modified poly(amide acid) solutions were made by adding the metal complex (20 mol% concentration) and stirring for at least 1 h. The final metal concentration was approximately 2.0 wt %, assuming complete imidization, complete conversion of the additive to the metal oxide, and no residual solvent.

The free-standing films were made by casting the modified and unmodified poly(amide acid) solutions onto a dust free glass plate at a thickness of 0.51 mm with a doctor blade. The film was then cured under either a dynamic air or nitrogen atmosphere at 80 °C for 20 min and at 100, 200, and 300 °C for 1 h each. Upon cooling, the films were removed from the glass plate using a razor blade to lift off the film. The side exposed to the cure atmosphere will be referred to as the atmosphere side in the subsequent discussion. The glass side will be the side of the film which was in contact with the glass plate during the cure.

Measurements. X-ray photoelectron spectroscopy data were obtained using a Perkin-Elmer Phi Model 530 ESCA system equipped with a magnesium anode (K$_\alpha$ = 1253.6 eV) operated at 400 W. The samples were attached to aluminum mounts using double stick transparent tape. The binding energies obtained from XPS spectra were all corrected by positioning the C(1s) photopeak of the aromatic polyimide backbone at 284.6 eV.

Transmission electron micrographs were taken with a Philips Model 420 scanning transmission electron microscope. The samples for TEM analysis were embedded in Polyscience ultralow viscosity resin and cured for eight hours at 70 °C. A Reichert-Jung ultramicrotome and a microstar diamond knife were then used to obtain cross sections of the samples having thicknesses of between 500 and 800 Å. These sections were then placed on 200-mesh copper grids for analysis.

Thermal analyses were performed using a Perkin-Elmer Model TGS-2 thermogravimetric system (TGA) and a Perkin-Elmer Model DSC-4 differential scanning calorimeter (DSC). The instruments were used in conjunction with the Perkin-Elmer System 4 thermal analysis data station (TADS). TGA analyses were conducted at a heating rate of 10 °C/min under a dynamic air or nitrogen atmosphere, and the results were used to determine the polymer decomposition temperature (PDT, i.e., temperature at which 10% weight loss occurred). DSC analyses were conducted at a heating rate of 10 °C/min under a nitrogen atmosphere in order to determine the glass transition temperature (T$_g$). Elemental analyses (iron and sulfur) were obtained by Galbraith Analytical Laboratories, Knoxville, TN.

Reflectance infrared spectra of the composite films in the 4000–400-cm^{-1} region were acquired using a Nicolet Model 510 FT-IR spectrometer. An attenuated total reflectance apparatus (ATR) with a zinc selenide crystal was used because the films were too thick for standard transmission mode. Each spectrum was the average of 1000 individual scans.

Results and Discussion

Physical Analysis of BDSDA/ODA Composite Films.

Five films have been the focus of this investigation. Nonmodified BDSDA/ODA films were cured in both air
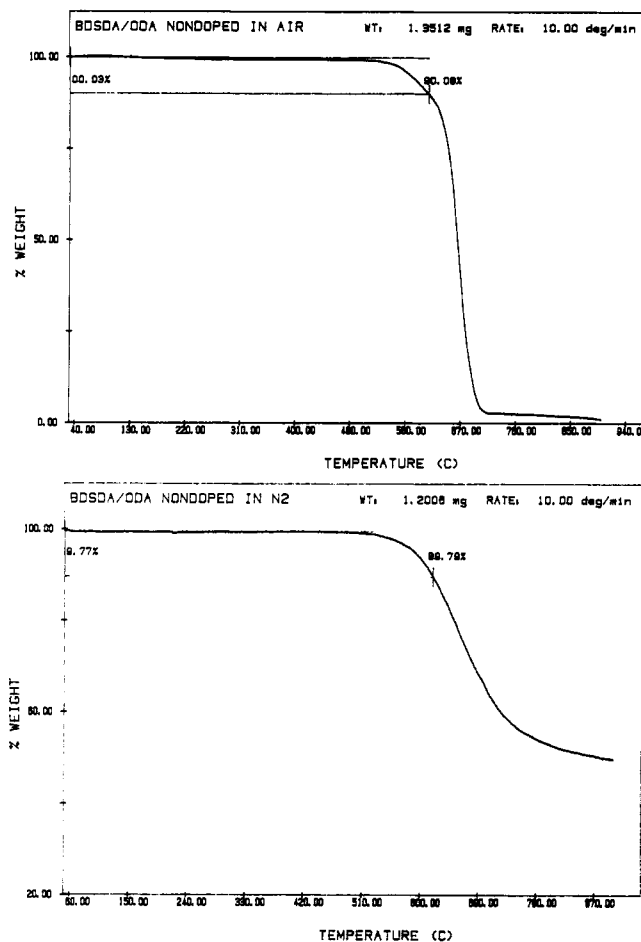

Figure 2. Thermogravimetric profiles of air-cured nonmodified film tested in air (top) and nitrogen (bottom).

and nitrogen atmospheres. Both films were pale yellow in color, very flexible, and creasible (Table 1). Two Fe-(acac)$_3$-modified composite films were synthesized at identical doping levels using an air and a nitrogen curing atmosphere. These two films were a deep red color. While the Fe(acac)$_3$-modified film cured in nitrogen was flexible and creasible like the nonmodified films, the Fe(acac)$_3$-modified film cured in air could not be creased without breaking. The last composite film used Fe(bzac)$_3$ as the additive and was cured only in air. It was surprisingly flexible and creasible like the nonmodified and both of the nitrogen-cured Fe(acac)$_3$-modified films.

Thermal data are summarized in Table 1 for the five films. Nonmodified films cured in either air or nitrogen lost only 50% of their weight upon reaching 900 °C when tested in a dynamic flow of nitrogen (Figure 2). When these two films were tested in a dynamic flow of air, they lost in excess of 90% of their weight by 900 °C. Fe(acac)$_3$-modified films cured in either air or nitrogen and the air-cured Fe(bzac)$_3$-modified film lost ~40% of their weight upon reaching 900 °C in a nitrogen test atmosphere (Figure
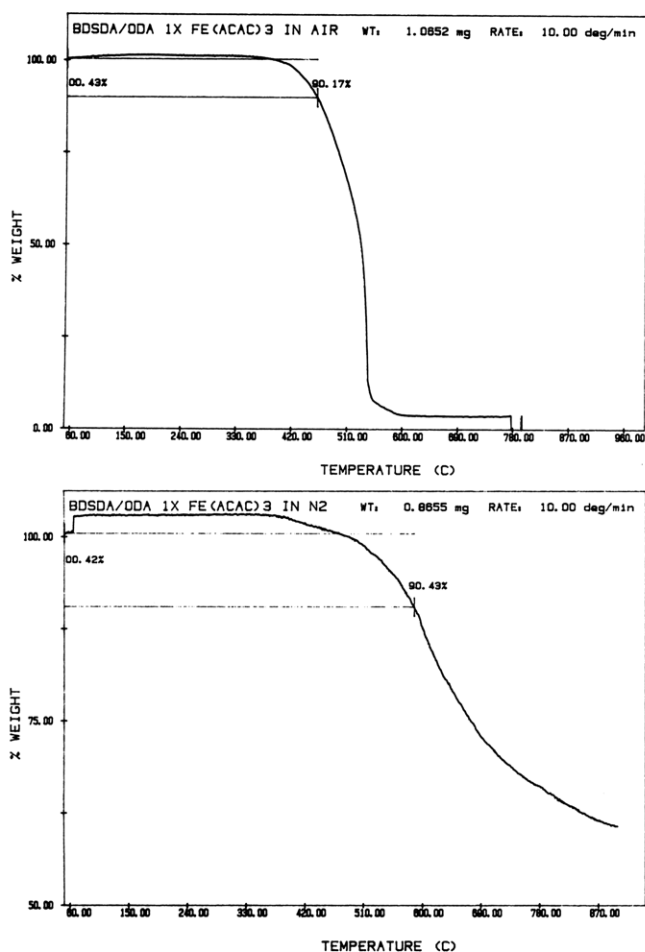
Metal-Modified Polyimide Composites

Chem. Mater., Vol. 6, No. 7, 1994 993

Figure 3. Thermogravimetric profiles of air-cured Fe(acac)$_3$-modified film tested in air (top) and nitrogen (bottom).

Table 2. Elemental Analysis of BDSDA/ODA Composite Films

film	wt % of sulfur in final film		wt % of iron in final film	
	actual	theoretical	actual	theoretical[a]
1	4.68	4.75		
2	4.78	4.75		
3	4.56	4.62	1.97	2.01
4	4.66	4.62	1.94	2.01

[a] Based on complete imidization, no residual solvent, and conversion to Fe$_2$O$_3$ in the case of iron-modified composites.
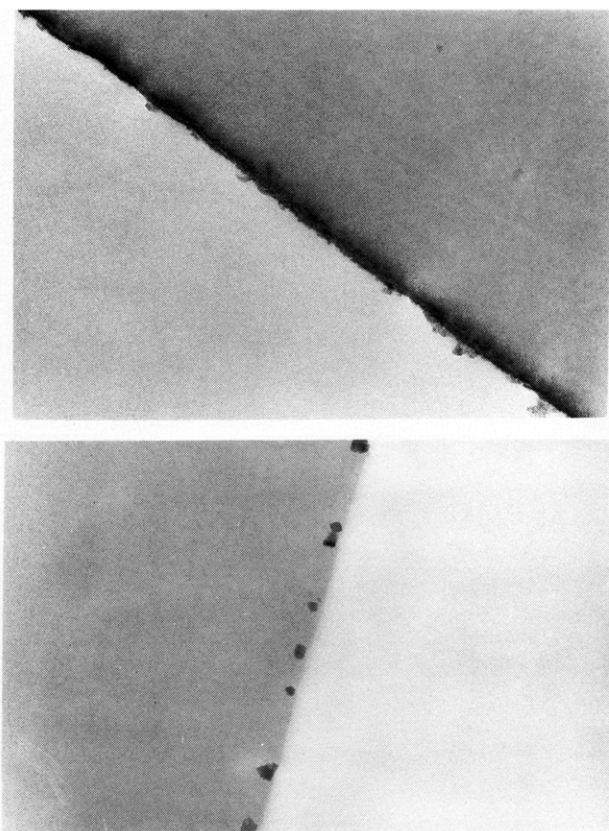

Figure 4. TEMs of atmosphere side surfaces of air-cured (bottom) and nitrogen-cured (top) Fe(acac)$_3$-modified composites.

3). When these films were tested in air, they also lost in excess of 95% of their weight by 900 °C.

Iron-modification caused only a slight decrease (30 °C) in the PDT compared to the nonmodified films when tested in nitrogen. The PDTs of the iron-modified composites measured in air, however, exhibited a significant reduction (150 °C) as compared to the nonmodified films. This dramatic decrease in the PDT of metal modified/polyimide composite has been observed elsewhere,[4,7] and the phenomena can probably be attributed to metal-catalyzed oxidative decomposition pathways in the composite.

T_g's of both air- and nitrogen-cured nonmodified films were identical (217 °C) and corresponded well with literature values (Table 1).[16] T_g's of the Fe(acac)$_3$-modified composites were higher than the nonmodified films (i.e., 261 °C, air-cured, and 248 °C, nitrogen-cured). The Fe(bzac)$_3$-modified film possessed a similar T_g of 250 °C. This increase may be due to the filler effect of the metal modifier thereby affording a stiffer composite film. On the other hand, the T_g for the sulfone version of this nonmodified polyimide (i.e., BDSO$_2$DA/ODA) is 260 °C.[16] Thus, the increase in T_g could be due to oxidation of the thioether moiety to a sulfone during the cure. For this oxidation to affect the T_g, however, it would have to occur completely throughout the film. This oxidation apparently did not occur throughout the film, as will be seen later.

Elemental analysis was performed on both the two nonmodified films and the two Fe(acac)$_3$-modified composites (Table 2). If the iron was completely converted to one of its oxides (i.e., Fe$_2$O$_3$, FeO, Fe$_3$O$_4$, FeOOH, or Fe(OH)$_3$) or if the iron remained unconverted (i.e., Fe(acac)$_3$), the expected weight percent of iron would be approximately 2% and sulfur would be 4.2%. The actual weight percent of iron found was 1.94 ± 0.19% for the modified composite cured in nitrogen and 1.97 ± 0.20% for the modified composite cured in air. While these values were too close to differentiate between an iron oxide and Fe(acac)$_3$, it was apparent that no iron was lost during the curing process. The actual weight percents of sulfur found for the nitrogen-cured composite and for the air-cured composite were also within the theoretical and found values for the undoped polymer which indicated that no polymer decomposition occurred and no sulfur was lost as SO$_2$.

Particle Distribution in BDSDA/ODA Composite Films. TEMs of the air-cured Fe(acac)$_3$-modified polyimide (Figure 4) composite film revealed that a few large particles (60 nm) were scattered along the atmosphere side of the film, forming a discontinuous surface layer, whereas only a few particles (80–100 nm in diameter) were observable in the bulk of the film. This observation is different from earlier work with non-sulfur-containing polyimides and Fe(acac)$_3$.[4] In that study many particles (20–80 nm) were observed in the bulk of the film compared to the few particles observed in this study. Since the
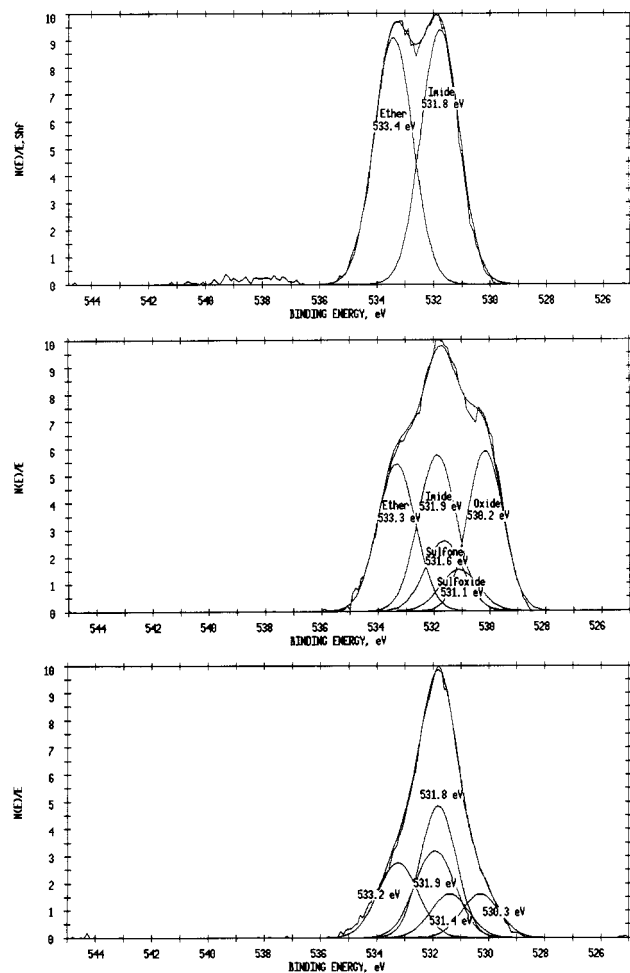
Figure 5. Oxygen 1s XPS photopeaks of the atmosphere surfaces of air-cured nonmodified (top), nitrogen-cured Fe(acac)$_3$-modified (middle), and air-cured Fe(acac)$_3$-modified (bottom) BDSDA/ODA films.

Figure 6. Sulfur 2p XPS photopeaks of the atmosphere surfaces of air-cured nonmodified (top), air-cured Fe(acac)$_3$-modified (middle), and nitrogen-cured Fe(acac)$_3$-modified (bottom) BDS-DA/ODA films.

majority of the added iron remained in the composite (>95%), it was hypothesized that the absence of a high population of iron-containing particles, observable by TEM, in the air-cured composite film may be due to the iron dopant residing throughout the film as highly dispersed particles (<10 Å). While this type of distribution is uncommon for metal-modified polyimides which do not contain a thioether moiety in the polymer backbone,[1] this distribution was observed as previously noted in the work by Porta et al.,[7] using copper and this same polyimide. TEMs of the air-cured Fe(bzac)$_3$-modified polyimide were similar to those of the Fe(acac)$_3$-modified polyimide insofar as bulk particles were concerned, but they did not contain any particles along the atmosphere surface.

For Fe(acac)$_3$-modified films cured under a nitrogen atmosphere, a continuous atmosphere side surface layer (60 nm) was observed (Figure 4), but again, only a few particles (80–100 nm) were found in the bulk of the film. A continuous surface layer is probably in the nitrogen-cured case as opposed to the air-cured case because the lack of molecular oxygen reduced the interaction between sulfur and iron during formation of the iron oxide along the surface of the film, thus allowing the iron oxide more mobility.

Surface Characterization of BDSDA/ODA Composite Films. The chemical state of the elemental components of the polyimide and the iron additive along the film surface were examined by XPS. Nonmodified
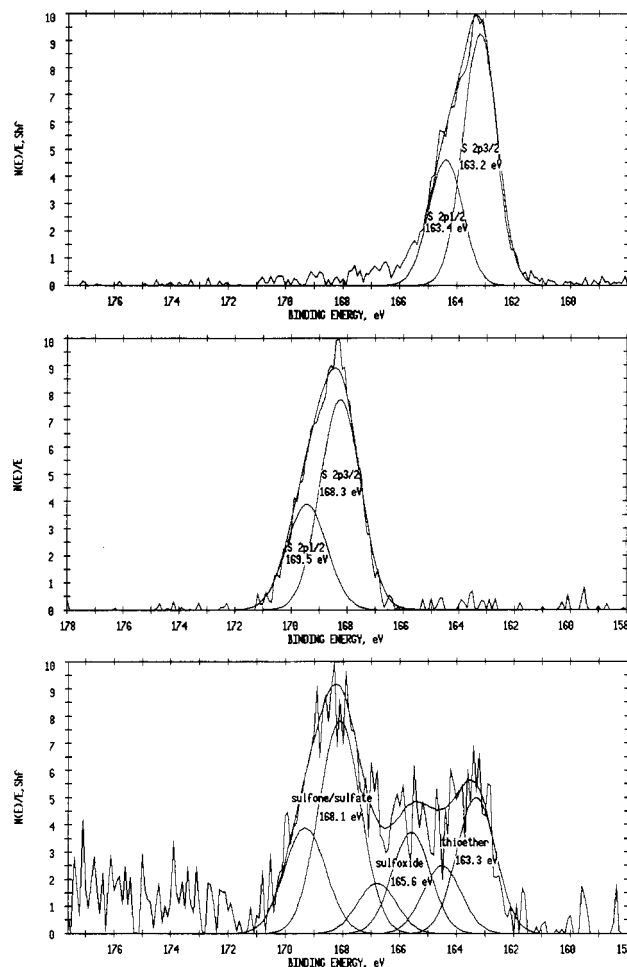
films were also examined for purposes of comparison. The spectra were curve resolved to yield sets of photopeaks consistent with the types and relative concentrations of elements present.

On the atmosphere side of the nonmodified air-cured BDSDA/ODA film, the nitrogen signal was at 400.0 (±0.1) eV corresponding to the imide nitrogen.[8] The oxygen 1s photopeak (Table 3) could be resolved into two signals: (a) 533.4 (±0.1) eV for an ether oxygen and (b) 531.8 (±0.1) eV for an imide oxygen[8] (Figure 5). The relative areas of these two peaks should have been in a ratio of 4:3 (imide: ether), but the ratio was closer to 3.2:3. The sulfur 2p photopeak could be resolved into the $2p_{1/2}$ and $2p_{3/2}$ components. The sulfur $2p_{3/2}$ binding energy of 163.3 (±0.1) eV corresponded to the thioether moiety[8,23] of the BDSDA part of the polyimide (Figure 6). The glass side surface of this film yielded similar results, as did both sides of the nonmodified nitrogen-cured film.

No oxidation of the sulfur was evident on either surface of air- or nitrogen-cured nonmodified films, which does not agree with the results of Burks and St. Clair,[21] who reported that the thioether in a polyimide composed of BDSDA and DDSO$_2$ was oxidized to the sulfone based upon infrared spectra. Alternatively, it is possible that the thioether sulfur was involved in an oxygen transfer

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Table 3. Binding Energies and Relative Concentrations of Oxygen, Sulfur, and Iron Species in the Composite Polyimide Films

film	oxygen						sulfur			iron
	ether	imide	sulfone	sulfoxide	hydroxide	oxide	sulfone	sulfoxide	thioether	
1	533.4	531.8							163.3	
	(3.9)	(4.0)							(0.9)	
2	533.6	532.0							163.1	
	(3.8)	(4.0)							(1.1)	
3	533.2	532.0	531.9		531.3	530.1	168.2			711.8
	(3.8)	(4.0)	(5.9)		(2.8)	(2.8)	(1.5)			712.7
4	533.4	531.9	531.7	531.4		530.2	168.2	165.8	163.3	711.2
	(3.8)	(4.0)	(2.2)	(0.5)		(4.0)	(0.5)	(0.3)	(0.3)	(2.2)
5	533.3	531.9	531.8		531.0	530.1	167.8	165.8	163.2	712.2
	(3.8)	(4.0)	(2.0)		(0.3)	(0.2)	(0.4)	(0.1)	(0.2)	(0.3)

a Values in parentheses were the relative concentrations of all the various functionalities based on four imide oxygens.
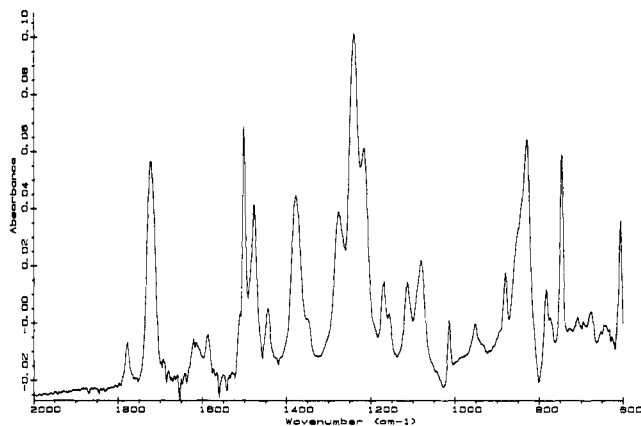
Figure 7. Reflectance IR spectrum of air-cured nonmodified film.

from the sulfone in the diamine which was subsequently re-oxidized. Reflectance IR spectra were obtained for the atmosphere side of the air-cured nonmodified film to determine if any oxidation could be observed via this technique (Figure 7). Absorption bands characteristic of imide rings were observed at 1775, 1720, 1375, and 705 cm⁻¹.[24] Other adsorption bands were observed at 1240 and 830 cm⁻¹ which represented an ether moiety[25] and para-substituted phenyl rings,[24] respectively. Characteristic absorption bands of sulfones, which occur at 1350–1300 and 1160–1120 cm⁻¹,[25] were not observed giving further evidence that the thioether sulfur was not oxidized in the nonmodified films.

The glass side surfaces of the iron-modified films appeared very similar to the nonmodified films via XPS. No iron was detected on this surface regardless of the additive or cure atmosphere used. The oxygen and sulfur photopeaks were similar to the photopeaks in the non-modified films, and no oxidized sulfur was evident. The XPS data for the atmosphere sides of the air-cured and nitrogen-cured iron-modified films, however, were significantly different from the nonmodified films. Thus, all further discussion of XPS data will refer exclusively to the atmosphere side of the films.

The chemical state of the iron seemed to be a function of cure atmosphere, while surface iron concentration was a function of the additive. In the air-cured Fe(acac)₃-modified film, iron was detected on the surface with a

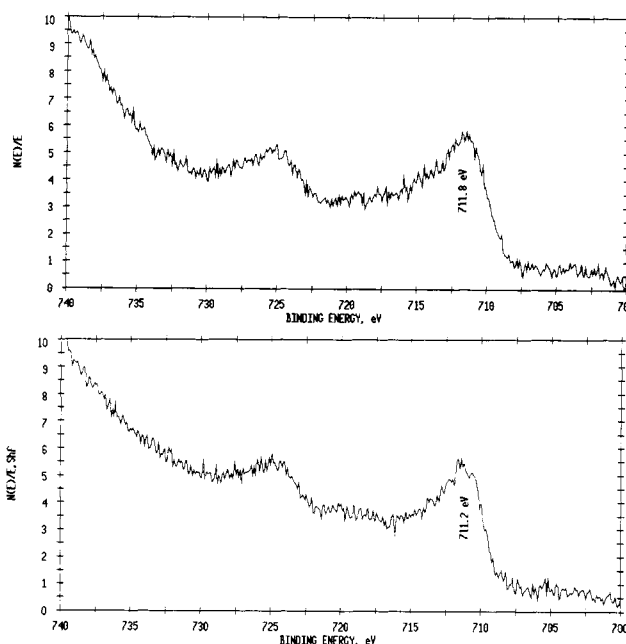**Figure 8.** Iron 2p XPS photopeaks of the atmosphere surfaces of air-cured Fe(acac)₃-modified (top) and nitrogen-cured Fe-(acac)₃-modified (bottom) BDSDA/ODA films.

$2p_{3/2}$ binding energy of 711.6 (±0.5) eV (Figure 8). The atomic concentration of iron was 2.9%. If the iron was dispersed evenly throughout the film, then an atomic surface concentration of only 0.5% (one iron atom for every four polymer repeat units) would be expected. XPS, therefore, indicates a slight enrichment of iron along the atmosphere surface as corroborated earlier by TEM analysis of that surface. The binding energy of the iron was indicative of iron in the +3 oxidation state.[26,27] The main iron signal, however, was too weak to ascertain any information from satellite structure. In the air-cured Fe-(bzac)₃-modified films the binding energy of the iron $2p_{3/2}$ photopeak was 712.0 (±0.1) eV and an atomic concentration of only 0.6% was observed which also agreed with previous TEMs results that showed no surface iron layer. Thus, changing the ligand from acac to bzac did not seriously affect the binding energy of the iron, but it did reduce the migration of iron to the surface. This phenomenon is most likely due to an increased inhibition to migrate due to the steric bulk of bzac compared to acac.

In the nitrogen-cured Fe(acac)₃-modified film, the iron $2p_{3/2}$ binding energy was 711.1 (±0.1) eV, while the atomic

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996 *Chem. Mater., Vol. 6, No. 7, 1994*

Ellison and Taylor

iron concentration was 3.3%, which was similar to that found for air-cured $Fe(acac)_3$-modified films. On the other hand, a difference in iron binding energy probably reflects a different form of iron oxide. The iron in the nitrogen-cured film has a binding energy similar to that of iron in Fe_2O_3 (710.8 ± 0.2 eV) with a corresponding oxygen 1s oxide peak at 530.1 (±0.1) eV.[27] The ratio of oxide oxygen to iron in this film was 1.8:1, which is close to that of Fe_2O_3 (1.5:1) and similar to results found by Bergmeister[4] in non-sulfur-containing iron-modified polyimide composites. The iron 3s binding energy was 93.4 (±0.2) eV and the $3p_{3/2,1/2}$ binding energy was 55.6 (±0.2) eV which agreed with the conclusion that the iron was predominantly present as Fe_2O_3.[27] The iron in both the $Fe(acac)_3$- and $Fe(bzac)_3$-modified air-cured films had binding energies closer to that of FeOOH (711.7 ± 0.2 eV) with corresponding oxygen 1s oxide photopeaks at 530.2 (±0.1) eV (oxide) and 531.2 (±0.2) eV (hydroxide).[27] The ratio of these oxygens to iron was approximately 1:1:1 (iron:oxide:hydroxide) which is appropriate for FeOOH. The air-cured $Fe(acac)_3$-modified composite had an iron 3s binding energy of 93.7 (±0.2) eV and a $3p_{3/2,1/2}$ binding energy of 56.1 (±0.2) eV, which supported the assignment of iron in the form of FeOOH.

The other major difference between the atmosphere sides of the iron-modified and nonmodified films involved the chemical state of the thioether sulfur. In the air-cured $Fe(acac)_3$-modified film, practically all of the thioether sulfur had been converted to a species with a binding energy of 168.2 (±0.1) eV (Figure 6) similar to what was observed in the work of Boggess.[8] Several sulfur species have binding energies in this region, such as sulfone ($-SO_2-$), sulfonate ($-SO_3-$), or sulfate ($-SO_4-$).[28,29] New sulfur $2p_{3/2}$ peaks were also observed in the air-cured $Fe(bzac)_3$-modified films at 165.8 (±0.1) eV and 167.8 (±0.1) eV that can be assigned to sulfoxide ($-SO-$) sulfur[23] and sulfone/sulfate sulfur,[28,29] respectively. The majority (55%) of the sulfur appeared as the sulfone/sulfate moiety in the bzac film, while the original thioether sulfur constituted 32% of the total amount of sulfur. The sulfoxide sulfur comprised the remaining 13%. These same two sulfur photopeaks were observed in the nitrogen-cured $Fe(acac)_3$-modified film but in different relative concentrations. As in the $Fe(bzac)_3$-modified films, approximately half of the sulfur was sulfone/sulfonate sulfur, while the remainder of the sulfur was equally divided between thioether and sulfoxide sulfur. The total atomic concentration of sulfur was the same (2.1% ± 0.1%) for both air- and nitrogen-cured $Fe(acac)_3$-modified films, which corresponded well with the expected atomic concentration of 2.0% for sulfur. The total atomic concentration of sulfur was slightly lower (1.5 ± 0.1%) in the $Fe(bzac)_3$-modified films.

The oxygen 1s photopeaks (Figure 5) were more difficult to curve resolve due to the amount of new oxygen species and the close proximity of their binding energies to existing photopeaks. The process used in analyzing the oxygen photopeaks consisted of fixing the ether and imide oxygen photopeaks in their known positions, peak widths, and relative concentrations as discussed for the nonmodified films. The ether photopeak was placed first since its position was separated from the other oxygen species. Next,
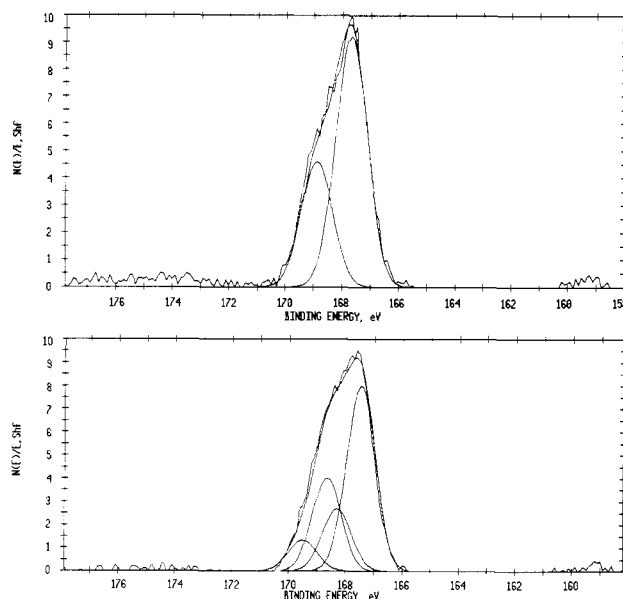
(28) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA 300 database;* John Wiley & Sons: New York, 1992; p 264.
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Figure 9. Sulfur 2p XPS photopeaks of the atmosphere surfaces of air-cured nonmodified (top) and air-cured $Fe(acac)_3$-modified (bottom) DSDA/ODA films.

photopeaks were placed at 530.1 and 531.8 (±0.1) eV to represent the contribution from iron oxide and imide oxygen, respectively.[26,27] The oxide photopeak was sufficiently separated from the other oxygen photopeaks so that it could be compared with the iron concentration. The final step was to locate the sulfone/sulfate oxygen at 531.7 (±0.1) eV[28] and the sulfoxide oxygen at 531.2 (±0.1) eV[23] based on literature values. By using the concentrations of the different sulfur species, the concentrations of the corresponding oxygen species were inferred. In the air-cured iron-modified films, an additional photopeak, equal in size to the oxide photopeak, was placed at 531.2 (±0.2) eV to represent the contribution of the hydroxide oxygen of FeOOH. The values in parentheses in Table 3 are the relative atomic concentrations of each element normalized to four imide oxygens. These new oxygen species, no doubt, contribute to the increase in total atomic oxygen concentration. The atomic concentration of oxygen was 30% for the air-cured and 25% for the nitrogen-cured $Fe(acac)_3$-modified films, which is considerably greater than the expected atomic concentration of 14%. The air-cured $Fe(bzac)_3$-modified films also had an increased oxygen atomic concentration of 21%. In summary, the sulfone/sulfate species was the major product in the air-cured $Fe(acac)_3$- and $Fe(bzac)_3$-modified films along with FeOOH, while Fe_2O_3 was more prevalent in the nitrogen-cured films with less sulfone/sulfate species.

To further confirm these assignments, air-cured nonmodified and $Fe(acac)_3$-modified films using a sulfone-containing monomer (DSDA) and ODA were examined. The sulfone sulfur photopeak in the nonmodified DSDA/ODA had a binding energy of 167.7 (±0.1) eV. The iron in the $Fe(acac)_3$-modified DSDA/ODA seemed to be in a similar state as the air-cured $Fe(acac)_3$-modified BDSDA/ODA, e.g., FeOOH, with a binding energy of 711.7 (±0.1) eV. The sulfur photopeak in the modified film had a binding energy of 167.5 (±0.1) eV, similar to that of the nonmodified film, but it was broader than the sulfur photopeak of the nonmodified film (Figure 9). When the curve fit for the nonmodified sulfur photopeak was used with the $Fe(acac)_3$-modified sulfur photopeak, the left or
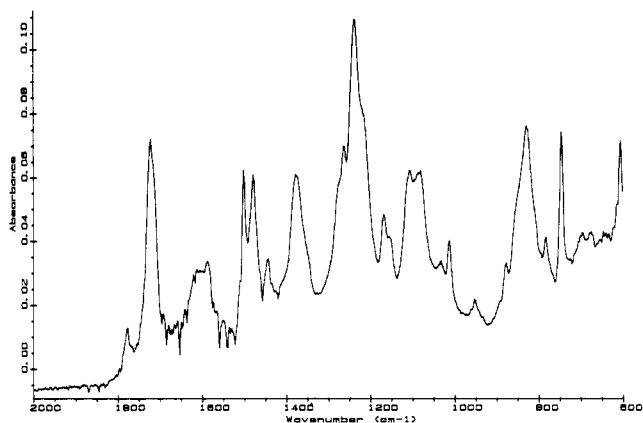
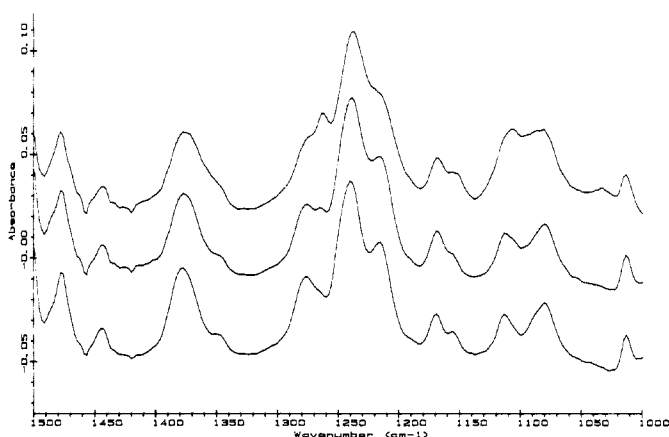**Figure 10.** Reflectance IR spectrum of air-cured Fe(acac)₃ modified film.

Figure 11. Reflectance IR spectrum of air-cured nonmodified film (bottom), air-cured Fe(acac)₃-modified (top), and nitrogen-cured Fe(acac)₃-modified (middle) BDSDA/ODA films.

higher binding energy side of the photopeak was not adequately covered. This area would be where sulfur that was more oxidized than sulfone would be located. Thus, this broadening could indicate further oxidation of sulfone to sulfonate or sulfate.

Reflectance IR spectroscopy was used to gain additional information on the chemical state of sulfur on the atmosphere side of the air-cured and nitrogen-cured Fe-(acac)₃-modified BDSDA/ODA films, (Figure 10). No absorption bands indicative of sulfone were observed. A new band was observed at 1270 cm⁻¹ in both composite films, but it was more prominent in the air-cured film. The air-cured film also had a new absorption band at 1030 cm⁻¹. These bands correspond to several possible species. A sulfate salt (RSO₄⁻M⁺) has a characteristic SO₂ absorption which often occurs as a doublet at 1250 and 1220 cm⁻¹.[30] The air-cured Fe(acac)₃-modified spectra showed the disappearance of a valley in the 1220-cm⁻¹ region that had been in the nonmodified film (Figure 11). An aromatic sulfate salt has a characteristic symmetric SO₂ stretch around 1040 cm⁻¹.[30] Sulfonic acid salts (RSO₃⁻M⁺) also have characteristic adsorption bands at 1250–1140 cm⁻¹ (asymmetric SO₃ stretch) and 1070–1030 cm⁻¹ (symmetric SO₃ stretch).[30] The actual position of absorption bands in both sulfate and sulfonic acid salts have been stated to be strongly influenced by the metal ion.[30] The adsorption band at 1030 cm⁻¹ could also be due to a sulfoxide SO
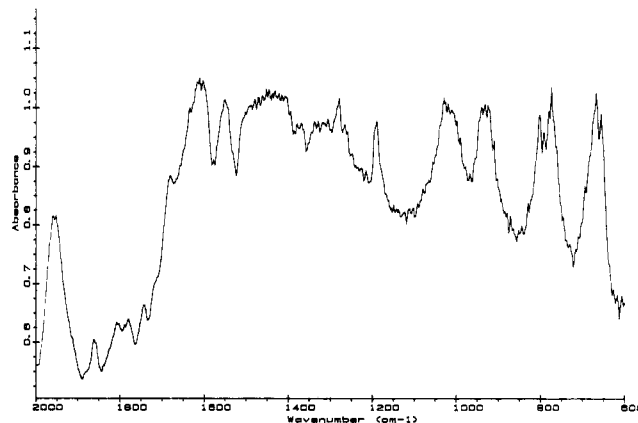

Figure 12. Diffuse reflectance IR spectrum of Fe(acac)₃.

stretch which usually occurs at 1060 cm⁻¹ in aromatic compounds.[30] From a comparison of the IR spectrum of Fe(acac)₃ (Figure 12) and that for Fe(acac)₃-modified film, it was apparent that no iron remained as Fe(acac)₃ along the surface of the film. Unfortunately, no characteristic adsorption bands of Fe₂O₃ and FeOOH were identified, although FeOOH is stated to absorb at 1026 cm⁻¹.[31]

From the XPS and IR data, it was evident that two reactions occurred along the atmosphere side during the thermal curing process: (a) conversion of the modifier to iron oxide and (b) oxidation of the thioether sulfur at least to sulfone and possibly either a sulfonate or sulfate. The extent of oxidation appeared to be dependent on the cure atmosphere used.

During the cure, it is hypothesized that water of imidization reacts with the modifier to form Fe(OH)₃ and the corresponding Hacac or Hbzac. Next, the thioether sulfur probably binds to the iron complex thereby trapping the iron in place. In the work by Bergmeister,[4] significant amounts of iron oxide migrated to the surface after only curing the non-sulfur-containing composite to 100 °C. In the air-cured Fe(acac)₃–BDSDA/ODA composite, however, iron oxide and oxidized sulfur were not observed after curing to 200 °C. No iron oxide particles were observed by TEM either. Thus, it appears that the sulfur traps the iron on a molecular scale.

The oxidation of the thioether was probably promoted by a transition-metal-catalyzed reaction with molecular oxygen. Both transition-metal oxides and transition-metal complexes, including M(acac)ₓ, have been observed to catalyze this reaction.[22,32] Apparently, the sulfur binds to the transition-metal which activates the complex for attack by oxygen. Both water and molecular oxygen have been used as sources of oxygen for this reaction.[22] The only source of oxygen available to the nitrogen-cured films would be from the water of imidization. Thus, the presence of the molecular oxygen is a probable explanation for why the thioether sulfur along the surface was completely oxidized in the air-cured Fe(acac)₃-modified film, while a mixture of products was the result in the nitrogen-cured Fe(acac)₃-modified film. The air-cured Fe(bzac)₃-modified film produced a mixture of products because there was no surface enrichment of iron to help catalyze the reaction as there was in the case of the Fe(acac)₃-modified film.

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(31) Schwertmann, U.; Cornell, R. M. *Iron Oxides in the Laboratory: Preparation and Characterization;* VCH Publishers, Inc.: New York, 1991; p 28.

(32) Mukhlenov, I. P.; Buzanova, G. N.; Parkhomova, E. A.; Selivanov, N. T.; Zayats, Y. N.; Saukhin, Z. A. *Chem. Abstr.* **1984,** *100,* 70336w.

The form of iron oxide produced appears to depend on the cure atmospheres used. A possible explanation for this behavior is that the oxidation of thioether sulfur by molecular oxygen, present in the air cure, created an ionic sulfonate/sulfate group that, in turn, coordinated to the iron during its conversion and prohibited the complete dehydration of $Fe(OH)_3$ to Fe_2O_3. Thus, the iron remained as FeOOH. Even after curing for an additional hour at 300 °C, the iron was still present as FeOOH. In the nitrogen-cured iron-modified composite, however, the only source of oxygen was from the water of imidization. It appears that the weaker oxidizing nature of water results in a covalent sulfonate (RSO_3R) or sulfate (RSO_4R) which does not coordinate as strongly to the iron and does not prevent conversion of $Fe(OH)_3$ to Fe_2O_3.

Other metal complexes were also examined to see how they would affect this thioether oxidation. $VO(acac)_2$ has been shown to be an excellent homogeneous catalyst for the oxidation of thioether sulfur.[22] Therefore, this complex was used in an air-cured polyimide composed of BTDA and ASD. The binding energy of the V 2p photopeak was 517.0 (±0.1) eV in the free-standing film which indicated that it resided as V_2O_5 and not $VO(acac)_2$ which has a binding energy of 515.1 eV.[33] The binding energy of the ASD thioether sulfur (167.6 (±0.1) eV) indicated that it had been oxidized. $Al(acac)_3$ was used as another modifier with air-cured BDSDA/ODA to examine the effects of a non-transition metal on thioether oxidation. The Al 2p binding energy of 74.2 (±0.1) eV in the resulting film indicated that the modifier was converted to Al_2O_3 and was no longer $Al(acac)_3$ (72.7 eV).[33] Some of the sulfur was converted to sulfoxide (20%) and sulfonate/sulfate (10%), but the majority (>70%) remained as the thioether sulfur. Thus, it appears that non-transition-metal complexes are not as good at catalyzing the oxidation reaction.

In summary, it is apparent that all of the surface sulfur was oxidized to sulfonate/sulfate. Only after etching down into the film was the original sulfur observed. The metal–sulfur interaction which is believed to prevent the aggregation of particles is probably direct chelation. The IR spectra shown in this study provide further evidence of oxidized sulfur species. These results indicate a change in the chemistry of the polyimide backbone which could be beneficial in adhesive situations. Since this oxidation has been observed on the glass side surface when silver is present,[34] it would seem that this reaction could occur when sulfur-containing polyimides were used with transition-metal substrates, such as steel or titanium. The resulting sulfonate/sulfate moiety could form stronger bonds to the metal substrate. The thioether itself may allow the polyimide to form stronger bonds to transition-metal substrates since the thioether appeared to be responsible for keeping the iron particles dispersed on a molecular scale in the composites. It is also possible that this oxidation of the thioether sulfur could damage the polyimide resulting in the formation of a weak boundary layer at the interface.

(33) *Handbook of X-Ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Perkin-Elmer Corporation: Eden Prairie, MN, 1979; pp 50–1, 70–1.

(34) Personal communication, Adley F. Rubira.