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Complex formation and degradation in poly(acrylonitrile-co-vinyl acetate) containing metal nitrates

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Abstract

Polymers containing metal-nitrates have been proposed as advantageous precursors for high temperature superconductors such as yttrium-barium-copper-oxide (YBCO). The advantage lies in using conventional polymer processing such as fiber spinning or microlithography before pyrolysis. This research investigated complex formation and degradation in poly(acrylonitrile-co-vinyl acetate) (P(AN-VA)) containing either yttrium nitrate (YN) or barium nitrate (BaN) and follows a similar investigation for copper nitrate. Complex formation was observed in P(AN-VA)/YN but not in P(AN-VA)/BaN. The exothermic nitrate degradation below the P(AN-VA)) cyclization temperature involved the release of NO_3, a reaction with the nitrile group that disrupted cyclization, and, for BaN, P(AN-VA) degradation. For a P(AN-VA)/nitrate ratio of 2/1 there was no cyclization and the degradation temperature was reduced by about 200 °C. The pyrolysis of P(AN-VA)/BaN yielded largely $BaCO_3$, which is likely to impede the formation of YBCO.

Keywords: Polyacrylonitrile; Metal nitrate; Pyrolysis

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1. Introduction

Certain ceramic oxides are high temperature superconductors (HTSC), exhibiting negligible resistances at temperatures above the boiling point of liquid nitrogen [1,2]. The HTSC containing copper, barium and yttrium ($YBa_2Cu_3O_{7-x}$) is known as YBCO (yttrium-barium-copper-oxide). The use of polymers containing metal-nitrates as HTSC precursors may provide a relatively simple and rapid method for producing HTSC fibers and ribbons. A HTSC precursor can be produced by dissolving a polymer and the appropriate metal-nitrates in a common solvent. The ratio of the metal atoms should be the same as their ratio in the desired HTSC phase. Complex formation is expected to enhance atomic level mixing of the metal ions and hinder recrystallization on solvent evaporation. The pyrolysis of a HTSC precursor should leave an amorphous metal oxide from which a crystalline HTSC phase can be formed [3]. Various polymers (poly(methacrylic acid), methylmethacrylate-methacrylic acid copolymers and cresol novolacs) have been used to produce HTSC precursors suitable for microlithography [4–8].

Polyacrylonitrile (PAN) and copolymers of acrylonitrile and vinyl acetate (P(AN-VA)) are commonly used for fiber-spinning and could yield spinnable HTSC precursors. P(AN-VA) has highly polar acrylonitrile groups that can coordinate with metal ions. The pyrolysis of PAN fibers under controlled conditions is used to produce carbon fibers and this could be used to advantage during the formation of HTSC fibers from HTSC precursor fibers. Polyacrylonitrile in an inert atmosphere is known to degrade through well-defined pyrolysis stages: Cyclization (250–350 °C) in which the adjacent nitrile groups form rings; Carbonization I (350–550 °C) in which the cyclic structure undergoes decomposition and carbonization; Carbonization II (above 550 °C) in which the cyclic structure undergoes further carbonization [9]. At high temperatures (above 550 °C) in an oxidative atmosphere PAN undergoes thermo-oxidative degradation.

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The initial phase of this work focused on complex formation and degradation in P(AN-VA) containing copper nitrate (CuN). CuN had a profound effect on P(AN-VA) degradation [10]. Fourier transform infrared spectroscopy (FTIR) revealed polymer coordination with the copper and nitrate ions. P(AN-VA)/CuN exhibited an exothermic peak from CuN degradation at about 170 °C (reaction 1-CuN). Reaction 1-CuN involved a significant mass loss of about 0.99 g/g_{NO_3} and a relatively constant heat per mass NO_3 (3500 J/g_{NO_3}). Reaction 1-CuN involved a nitrile group reaction, disrupting cyclization and causing a significant decrease in heat per mass from cyclization at about 290 °C (reaction 2-CuN) with CuN content. The addition of CuN to P(AN-VA) yielded a significant reduction in thermal stability and a decrease in the thermo-oxidative degradation temperature. The mass loss for thermo-oxidative degradation for P(AN-VA)/CuN of 0.61 $g/g_{P(AN-VA)}$ was similar to that for the neat polymer, 0.65 $g/g_{P(AN-VA)}$. This paper describes complex formation and degradation for P(AN-VA) containing either yttrium nitrate (YN) or barium nitrate (BaN).

2. Experimental methodology

2.1. Materials

The P(AN-VA) used was a commercial copolymer (Cytec Industries) with 1 vinyl acetate unit per 45 acrylonitrile units and a viscosity average molecular weight of 150,000 g/mol. Yttrium nitrate pentahydrate ($Y(NO_3)_3{\cdot}5H_2O$) was supplied by Aldrich, barium nitrate ($Ba(NO_3)_2$) was supplied by Merck, and copper nitrate 2.5 hydrate ($Cu(NO_3)_2{\cdot}2.5H_2O$) was supplied by Riedel de Haën. The solvent used was dimethylformamide (DMF) (Aldrich).

2.2. P(AN-VA)/nitrate

A P(AN-VA)/DMF weight ratio of 1/17 was used for all the solutions. This ratio was chosen as one that would provide a relatively high polymer concentration given the limited solubility of P(AN-VA). Solutions of P(AN-VA) in DMF were slightly turbid at 25 °C. A clear yellow solution resulted after heating to 60 °C. Solutions of P(AN-VA) and the metal nitrate in DMF were prepared by dissolving the nitrate in DMF, adding the P(AN-VA) at 25 °C and then heating to 60 °C. The solution of CuN was blue and it turned green on adding P(AN-VA) and heating to 60 °C. The colors of the P(AN-VA) solutions containing either YN or BaN were similar to that of the P(AN-VA) solution. The P(AN-VA)/nitrate weight ratios used were 10/1, 4/1 and 2/1. The materials cast from these solutions will be referred to as ‘10/1’, ‘4/1’ and ‘2/1’, respectively. Films 10–100 μm thick were obtained by casting the solutions onto glass plates and then drying at 60 °C for a few days. Powders were made by grinding the films using a mortar and pestle. This paper investigates P(AN-VA)/YN, P(AN-VA)/BaN and P(AN-VA)/(Y,Ba,Cu)N with Y:Ba:Cu = 1:2:3. The investigation of P(AN-VA)/CuN was described in a previous paper [10].

The number of monomer units per metal atom and the number of monomer units per nitrate group are listed for the various compositions in Table 1. For a given composition (10/1, 4/1 or 2/1) the number of monomers per nitrate group is about the same for YN, BaN and CuN. There is a somewhat larger variation in the number of monomers per metal atom among the different nitrates. P(AN-VA) containing all three nitrates in the proportions needed for YBCO has an overall metal concentration and an overall nitrate concentration similar to those for P(AN-VA) containing a single nitrate for a given polymer to metal nitrate ratio (Table 1).

2.3. Characterization

Differential scanning calorimetery (DSC) was performed from 25 to 350 °C at 10 °C/min both in nitrogen and in dry air (Mettler DSC 821). Materials were exposed to a specific elevated temperature for FTIR characterization by heating in the DSC to that temperature at 10 °C/min both in nitrogen and in dry air. Simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) was performed from 25 to beyond 800 °C at 5 °C/min in flowing dry air at a rate of 30 cc/min (Setaram 92-16.18). TGA/DTA in an inert atmosphere yielded a carbonaceous residue that adhered to the holders and to the crucible and that clogged all the instrument’s gas outlets, leading to significant errors in the on-line measurement of sample mass. The differential thermal gravimetry (DTG) thermograms were derived from the TGA data using the supplied software.

FTIR was performed in transmission through thin films or through KBr pellets containing 1% by weight of the material (Nicolet Impact 400). The effects of nitrate content and the effects of heating to elevated temperatures were followed by comparing specific band heights normalized by the height of the CH stretching band at 2925 cm^{-1}. The CH band at 2925 cm^{-1} was chosen as the normalization band since it is a distinct band that appears in all the spectra. Other bands which may have been used for normalization were obscured on the addition of metal salts. The normalization can only be used to draw general qualitative trends from the FTIR data since the reactions at elevated temperatures (cyclization and degradation) also affect the CH groups. The ring strain in the first stage of cyclization would shift and broaden the normalization band and the deprotonation in the second stage of cyclization would reduce the CH content. The effects that changes to the CH groups have on the normalization process must be kept in mind when comparing materials with different degrees of cyclization.

Table 1
Monomer units per metal atom and monomer units per nitrate group for the different nitrates and compositions

	10/1		4/1		2/1	
	Metal	Nitrate	Metal	Nitrate	Metal	Nitrate
CuN	42	21	17	8	8	4
YN	66	22	26	9	13	4
BaN	47	24	19	9	9	5
YN + 2BaN + 3CuN:						
—Total (Y + Ba + Cu)	48	22	19	9	10	4
—Individual (Y/Ba/Cu)	285/143/95	22	114/57/38	9	57/29/19	4

2.4. HTSC precursor pyrolysis and HTSC characterization

The HTSC precursor used was P(AN-VA)/(Y,Ba,Cu)N = 2/1 with Y:Ba:Cu = 1:2:3. The precursor was characterized as a powder and as a film. The powder was produced as described above. The film was produced by spin-casting the precursor solution on a strontium titanate substrate and drying at 170 °C for two hours. The spin-casting was repeated five times to produce a relatively thick film. The pyrolysis process was based on the results of this P(AN-VA)/nitrate degradation investigation and then optimized for YBCO production. The precursor pyrolysis conditions were: heating from room temperature to 450 °C at 5 °C/min in nitrogen; holding at 450 °C for 2 h in nitrogen; heating to 700 °C at 5 °C/min in nitrogen; heating to 950 °C at 10 °C/min in oxygen; holding at 950 °C for 1.5 h in oxygen; slowly cooling to 450 °C at 3 °C/min in oxygen; holding at 450 °C for 3 h in oxygen; slowly cooling to room temperature at 3 °C/min in oxygen.

X-ray diffraction (XRD) was carried out using a grazing angle (Θ = 3) and a Ni-filtered Cu Kα X-ray beam excited at 40 keV and 40 mA (Philips PW 1840). Step scans were made with 0.02° steps and a 12 s exposure per step.

3. Results and discussion

3.1. Degradation of CuN, YN and BaN

The TGA of CuN, YN and BaN are compared in Fig. 1. CuN undergoes the most rapid degradation at a relatively low temperature, with DTG peaks at 193 and 264 °C. The 0.33 g/g_{CuN} residual mass is consistent with the 0.34 g/g_{CuN} residual mass calculated for the oxidation of CuN to CuO. The CuN degradation process dominated the degradation of P(AN-VA)/CuN [10]. On heating to 335 °C, YN loses hydration water in several stages becoming $Y(NO_3)_3$ and $Y(OH)(NO_3)_2$ and exhibiting several DTG peaks [11]. Degradation continues, with a DTG peak at 377 °C for the formation of $YONO_3$, and a DTG peak at 508 °C for the formation of Y_2O_3 [11]. The 0.30 g/g_{YN} residual mass is consistent with the 0.31 g/g_{YN} residual mass calculated for the oxidation of YN to Y_2O_3. The degradation of YN is less rapid than that of CuN and a large part of the degradation occurs above the P(AN-VA) cyclization temperature. BaN is considerably more thermally stable than CuN and YN, undergoing degradation at high temperatures with a DTG peak at 715 °C. The 0.59 g/g_{BaN} residual mass is consistent with the 0.59 g/g_{BaN} residual mass calculated for the decomposition of BaN to BaO. The relative thermal stability of BaN alone, however, stands in contrast with its significant effect on P(AN-VA) degradation.

3.2. P(AN-VA)/YN

3.2.1. Molecular structure

The FTIR spectra of P(AN-VA), YN and 2/1 containing YN are seen in Fig. 2. The major absorption bands for P(AN-VA) are CH twisting deformation at 1250 cm^{-1}, CH in-plane deformation at 1384 cm^{-1}, CH_2 bending at 1453 cm^{-1}, C=O carbonyl stretching for VA at 1740 cm^{-1}, C≡N stretching at 2243 cm^{-1}, CH_3 stretching at 2856 cm^{-1} and CH stretching at 2925 cm^{-1} [12]. The spectrum for P(AN-VA) also reveals the presence of residual DMF, characterized by distinctive bands at 659 cm^{-1} (C=O wag) and 1669 cm^{-1} (O=C–NH_2 stretching). The major absorptions for the NO_3 in YN are 751 and

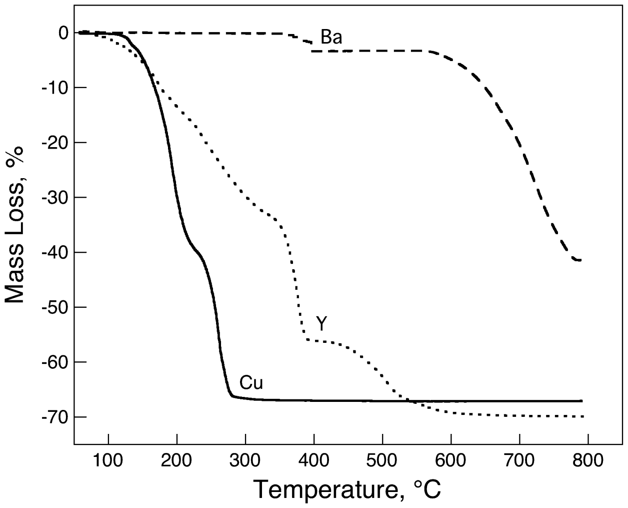

Fig. 1. TGA of CuN, YN and BaN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

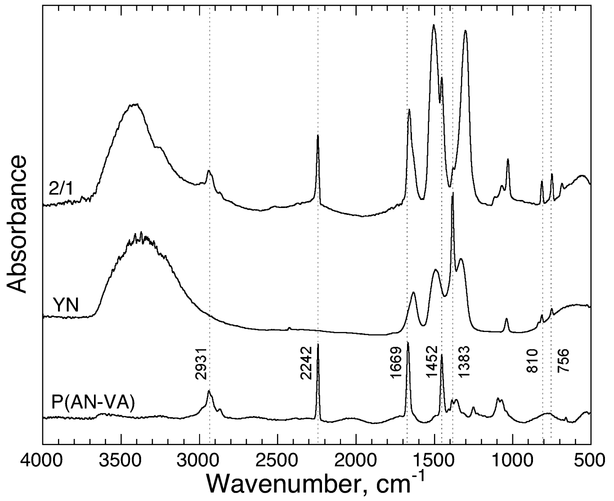

Fig. 2. FTIR spectra of P(AN-VA) as-cast, YN as-received and 2/1(YN) as-cast.

815 cm^{-1} (out of plane bend), 1040 cm^{-1} (symmetric stretching) and the dominant peak at 1384 cm^{-1} (asymmetric stretching) [12,13]. The bands at about 3371 cm^{-1} can be attributed to OH from the hydration water and to moisture in the KBr pellet.

The spectrum for 2/1 has bands associated with P(AN-VA) (1453, 2243 and 2925 cm^{-1}), with residual DMF (1669 and 659 cm^{-1}) and with YN (751 and 815 cm^{-1}) as well as some unusual features. The major absorption band for NO_3 at 1383 cm^{-1} for YN is split into two bands (1499 and 1298 cm^{-1}). This splitting, when observed for P(AN-VA)/CuN, was related to a change in the NO_3 vibration mode caused by complex formation between the metal ion (M^+) and the nitrile group: $C{\equiv}N\cdots M^+$[10,13,14]. However, unlike P(AN-VA)/CuN, P(AN-VA)/YN does not exhibit a band at 2300 cm^{-1} that would indicate coordination between the nitrile group and the metal ion [13,15].

The variation of selected normalized FTIR band heights with YN content is seen in Fig. 3. The normalized intensity of the C≡N stretch at 2243 cm^{-1} remains relatively constant and independent of the YN content. This indicates that the nitrile groups in the P(AN-VA)/YN have not chemically reacted during mixing and drying. The normalized intensity of the band associated with NO_3 at 815 cm^{-1} increases with the nitrate content.

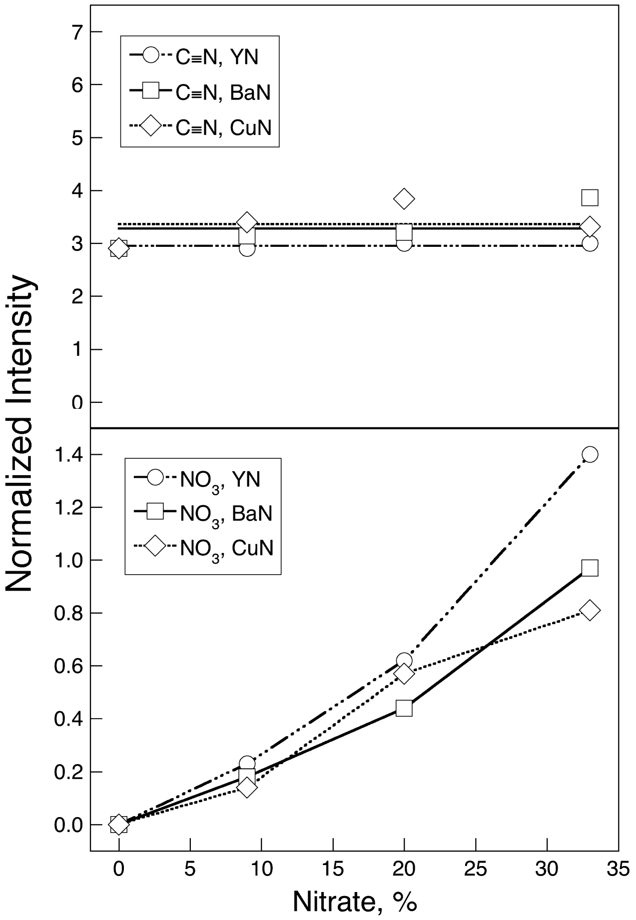

Fig. 3. Normalized FTIR intensities for C≡N (2243 cm^{-1}) and NO_3 (815 cm^{-1}) from the spectra of P(AN–VA)/YN, P(AN–VA)/BaN and P(AN–VA)/CuN (all as-cast): variation with nitrate content.

3.2.2. Degradation

DSC thermograms run in air for P(AN-VA)/YN are seen in Fig. 4 (the DSC runs in nitrogen were quite similar). A summary of the DSC data is presented in Table 2. In P(AN-VA), cyclization yields an exothermic peak at 289 °C with a heat of 690 J/g$_{\mathrm{P(AN\text{-}VA)}}$ (480 J/g$_{\mathrm{P(AN\text{-}VA)}}$ when run in nitrogen). The addition of a small amount of YN (10/1) yields significant changes in the thermogram. An exothermic peak, Reaction 1-YN, appears at about 244 °C, below the cyclization temperature. The heat per mass sample of this peak and the peak temperature increase with YN content. For 4/1(YN) and 2/1(YN), Reaction 1-YN has a heat per mass NO_3 of about 3400 J/g$_{NO_3}$ (210 kJ/mol$_{NO_3}$), whether run in air or in nitrogen. The thermograms for P(AN-VA)/YN (Fig. 4) exhibit at least two peaks at higher

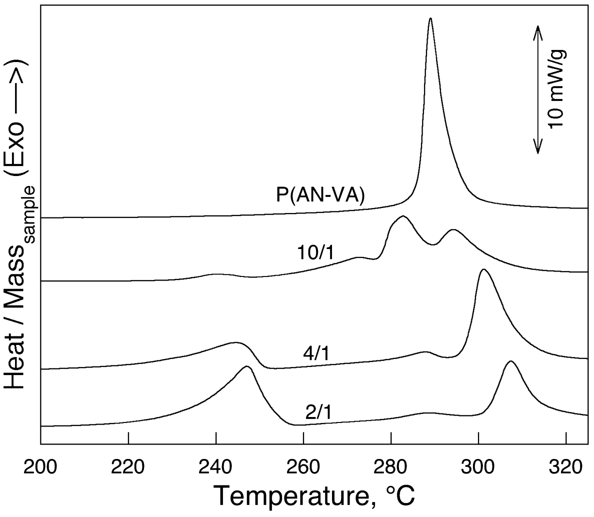

Fig. 4. DSC thermograms for P(AN-VA)/YN performed from 25 to 350 °C at 10 °C/min in air.

Table 2
P(AN-VA)/YN data from the DSC, DTA, TGA and DTG thermograms in air

	P(AN-VA)	P(AN-VA)/YN		
		10/1	4/1	2/1
	Evaporation	Evaporation		
DTG peak (°C)	185	84	85	90
Mass loss (%)	5.5	4.3	5.0	5.7
		Reaction 1-YN		
DSC peak (°C)	–	239	245	247
Heat (J/g_{sample})	–	27	349	581
Heat (J/g_{NO_3})	–	589	3421	3471
DTA peak (°C)	–	–	240	242
DTG peak (°C)	–	–	236	239
Mass loss (%)	–	–	9.3	15.0
Mass loss (g/g_{NO_3})	–	–	0.91	0.88
	Cyclization	Reaction 2-YN		
DSC peak (°C)	289	283	288	288
Heat (J/g_{sample})	690	177	48	45
Heat (J/$g_{P(AN\text{-}VA)}$)	690	195	60	68
DTA peak (°C)	263	266	278	280
DTG peak (°C)	270	267	275	276
Mass loss (%)	5.6	5.3	4.0	3.8
Mass loss (g/$g_{P(AN\text{-}VA)}$)	0.056	0.058	0.058	0.057
		Reaction 3-YN		
DSC peak (°C)	–	295	301	307
Heat (J/g_{sample})	–	86	567	305
DTA peak (°C)	–	279	296	296
DTG peak (°C)	–	277	295	299
Mass loss (%)	–	5.7	5.3	3.3
	Carbonization I	Reaction 4-YN		
DTA peak (°C)	459	410	–	–
DTG peak (°C)	414	414	–	–
Mass loss (%)	15.0	3.0	–	–
	Oxidation	Reaction 5-YN		
DTA peak (°C)	767	647	574	566
DTG peak (°C)	712	576	521	509
Mass loss, %	65.0	66.0	59.4	52.2
Mass loss (g/$g_{P(AN\text{-}VA)}$)	0.65	0.73	0.65	0.57
	850 °C	850 °C		
Residual mass (%)	0.7	3.2	6.1	9.4
Residual mass (g/g_{YN})	–	0.35	0.31	0.28

temperatures. The peak at about 286 °C can be associated with cyclization (reaction 2-YN). The peak at about 301 °C can be associated with one of the stages in YN degradation (reaction 3-YN). Both peak temperatures increase with YN content. The size of the peak at about 286 °C decreases with YN content while the size of the peak at about 301 °C increases with YN content. 10/1 also exhibits a small peak at 272 °C which is most likely related to the cyclization peak at 283 °C.

The behavior of P(AN-VA)/YN is in some ways similar to that of P(AN-VA)/CuN [10]. P(AN-VA)/CuN exhibited two DSC peaks. FTIR and thermal analyses indicated that the degradation of CuN at about 170 °C (reaction 1-CuN) involved the release of NO_3 and reaction with the nitrile groups. The heat per mass NO_3 of Reaction 1-CuN was 3500 J/g_{NO_3} (220 kJ/mol_{NO_3}), similar to that found for Reaction 1-YN. This indicates that Reaction 1-YN is a YN degradation reaction involving the release of NO_3. There was a cyclization reaction in P(AN-VA)/CuN at about 289 °C (reaction 2-CuN). The significant reduction in Reaction 2-CuN with CuN content indicated that Reaction 1-CuN disrupted cyclization. Similarly, the reduction in Reaction 2-YN with YN content indicates that Reaction 1-YN disrupts cyclization. Reaction 3-YN at about 310 °C is a further stage in the multi-stage degradation of YN. There is no equivalent exotherm for P(AN-VA)/CuN since CuN exhibits a rapid, one-stage decomposition.

FTIR spectra for P(AN-VA) and 2/1(YN) after exposure to elevated temperatures are seen in Fig. 5. Heating to 260 °C goes beyond Reaction 1-YN but is below Reaction 2-YN, while heating to 325 °C goes beyond Reaction 3-YN. The spectra for P(AN-VA) heated to 260 and 325 °C exhibit distinct bands at about 2242 cm^{-1} (C≡N) and at about 1615 cm^{-1} (C=N). Both P(AN-VA) and 2/1(YN) exposed to 325 °C exhibit a band at 2190 cm^{-1} that can be attributed to an imino nitrile structure which is created when cyclization is blocked by the VA group [16]. For 2/1(YN) exposed to elevated temperatures (Fig. 5) there is no trace of the strong NO_3 bands at 1299 and 1489 cm^{-1} that were seen for the as-cast 2/1(YN) (Fig. 2). The disappearance of the NO_3 bands indicates that NO_3 has been degraded on exposure to 260 °C.

The changes in relative intensity for C≡N and C=N shown in Fig. 6 are qualitative and dependent on the normalization band, but the trends are quite clear. The relative intensities of C≡N decrease with temperature while the relative intensities of C=N increase with temperature.

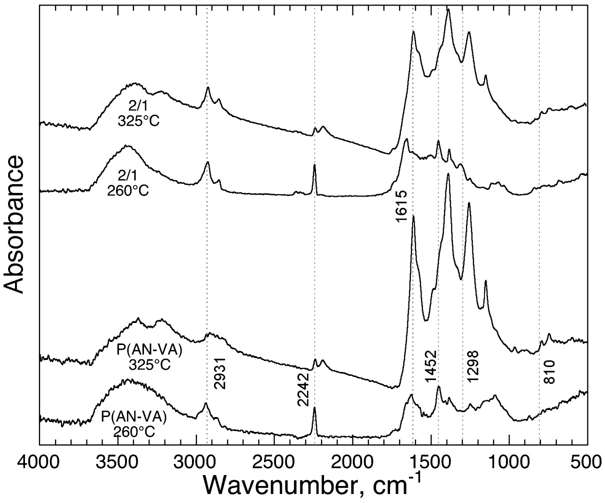

Fig. 5. FTIR spectra of P(AN-VA) and 2/1(YN) after exposure to either 260 or 325 °C.

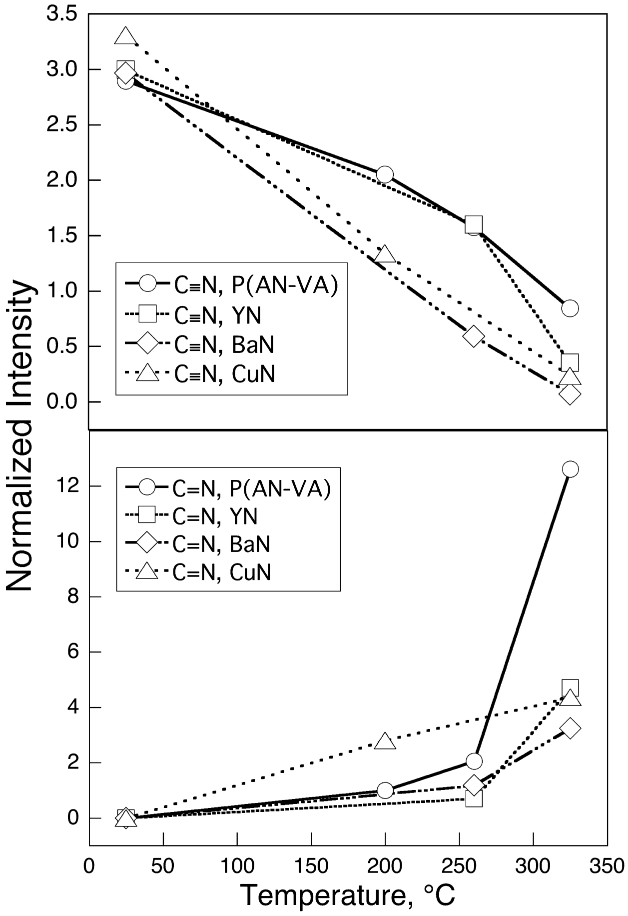

Fig. 6. Normalized FTIR intensities for $C\equiv N$ (2243 cm^{-1}) and $C{=}N$ (1615 cm^{-1}) from the spectra of P(AN-VA) and 2/1(YN, BaN or CuN): variation with temperature.

Surprisingly, the decrease in $C\equiv N$ and increase in $C{=}N$ on exposure to 260 °C are similar to those for P(AN-VA). The higher rate of decrease in $C\equiv N$ and higher rate of increase in $C{=}N$ for 2/1(CuN) may reflect the ability of copper to catalyze reactions with the nitrile group [10,17]. The relatively strong $C{=}N$ for P(AN-VA) exposed to 325 °C results from cyclization. Reaction 1-YN disrupts cyclization and yields the relatively low $C{=}N$ content for 2/1(YN) exposed to 325 °C (Fig. 6). The qualitative trends from the changes in the normalized heights of the bands associated with the cyclized structure are also clear (Fig. 7). There is a decrease in normalized band height on the addition of small amounts of YN (10/1) and the normalized band height continues to decrease with increasing YN content. The more rapid decrease in $C\equiv N$ at 325 °C for low CuN concentrations reflects the ability of Cu to catalyze nitrile reactions. The relatively large amount of $C{=}N$ at 325 °C for low CuN concentrations is the product of these nitrile group reactions.

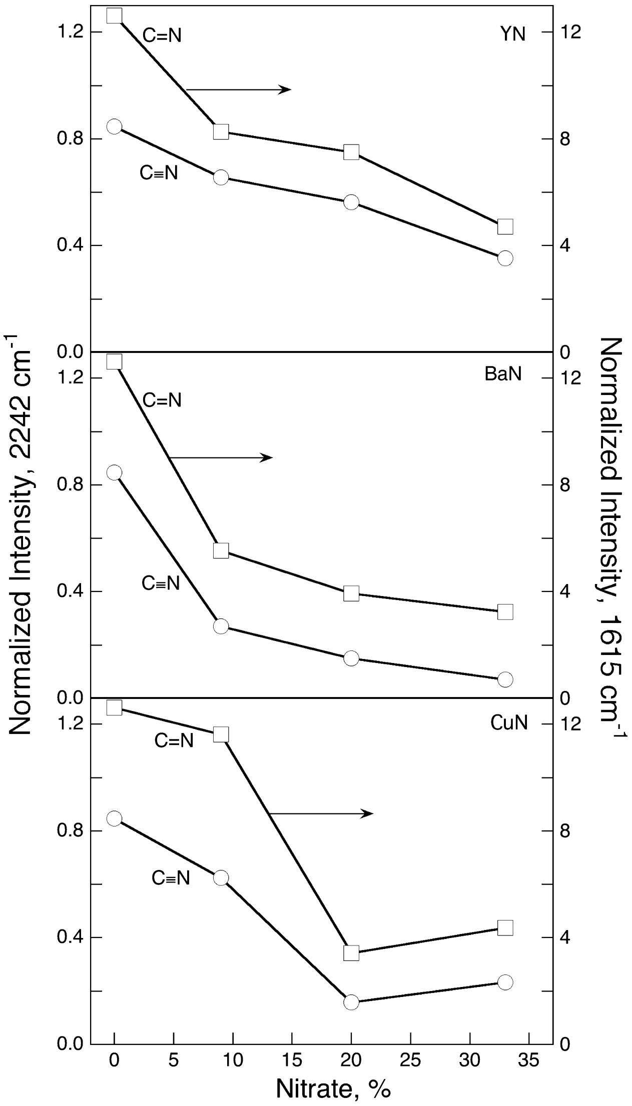

Fig. 7. Normalized FTIR intensities for $C\equiv N$ (2243 cm^{-1}) and $C{=}N$ (1615 cm^{-1}) from the spectra of P(AN-VA)/YN, P(AN-VA)/BaN and P(AN-VA)/CuN exposed to 325 °C: variation with nitrate content.

The DTA, TGA and DTG thermograms for P(AN-VA)/YN in Figs. 8–10, respectively, extend the thermal analysis beyond 350 °C. A summary of the DTA, TGA and DTG data is presented in Table 2. For Reactions 1-YN, 2-YN and 3-YN, the DTA and DTG peaks are in good agreement with the DSC peaks (with the small differences reflecting the differences in heating rates and techniques). The correspondence between the DTA and DTG peaks indicates that the exothermal reactions involve mass loss. PAN is known to bond strongly to DMF and is even capable of forming complexes by dipolar bonding [18]. FTIR has shown that residual DMF is still present in P(AN-VA) even following exposure to 200 °C [10]. The P(AN-VA) DTG peak at 185 °C is, therefore, ascribed to the evaporation of residual DMF. There is a very small endothermic DSC peak (not discernable in Fig. 4) that corresponds to this process. P(AN-VA)/YN exhibits a DTG peak from the evaporation of hydration water at about 86 °C (Table 2). The degradation in Reaction 1-YN involves a significant mass loss that increases with YN content. The mass loss per mass NO_3 for Reaction 1-YN, about 0.90 g/g_{NO_3}, is associated with the heat of 3400 J/g_{NO_3} and is similar to the mass loss in

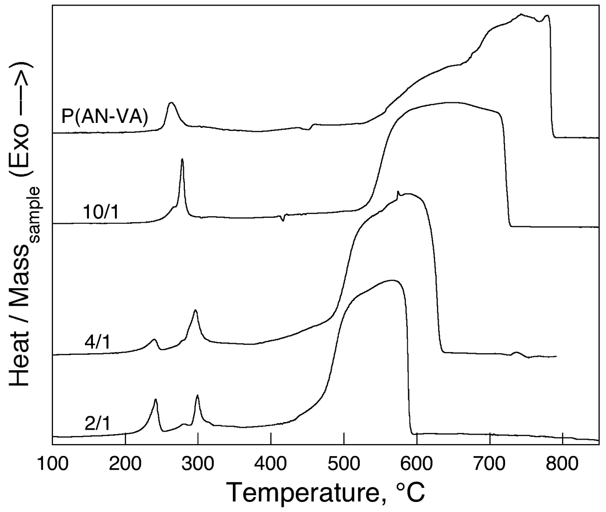

Fig. 8. DTA thermograms for P(AN-VA)/YN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

P(AN-VA)/CuN. Reaction 1-YN for 10/1 was minor, with a very small DSC peak and no discernable DTA or DTG peaks. The mass loss per mass P(AN-VA) for Reaction 2-YN is about 0.058 $g/g_{P(AN-VA)}$ is similar to the 0.056 $g/g_{P(AN-VA)}$ mass loss in P(AN-VA) cyclization.

P(AN-VA) exhibits a minor peak at about 431 °C from carbonization of the cyclized structure. Reaction 4-YN for 10/1, with a minor peak at 412 °C, most likely reflects a similar carbonization reaction. No corresponding reaction is observed at higher YN contents. Thermo-oxidative degradation in P(AN-VA) yields a DTA exotherm from 550 to 800 °C, with a peak at about 740 °C and a mass loss of 0.65 $g/g_{P(AN-VA)}$. Reaction 5-YN is the corresponding oxidation reaction and it exhibits a similar mass loss, about 0.65 $g/g_{P(AN-VA)}$. The initiation temperature, peak temperature, and peak width for Reaction 5-YN decrease with YN content. Reaction 5-YN for 2/1(YN), from 450 to 600 °C, has a peak at about 540 °C. YN significantly accelerates P(AN-VA) degradation, with 2/1(YN) reaching a constant residual mass at 600 °C, rather than at 800 °C. The residual mass of about 0.31 g/g_{YN} (Table 2) is consistent with the 0.31 g/g_{BaN} residual mass calculated for the oxidation of YN to Y_2O_3.

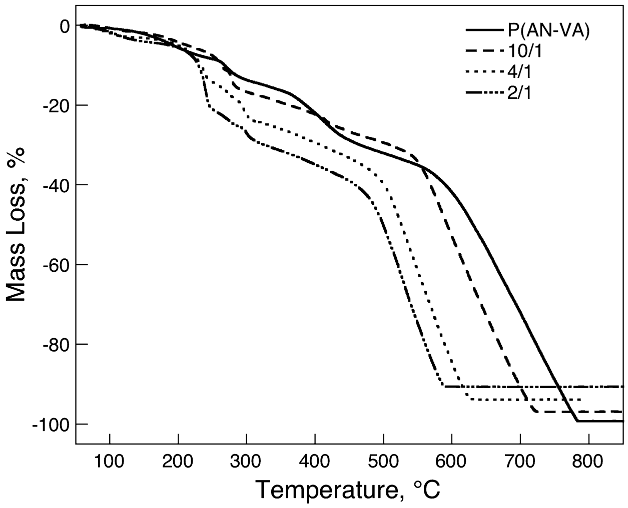

Fig. 9. TGA for P(AN-VA)/YN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

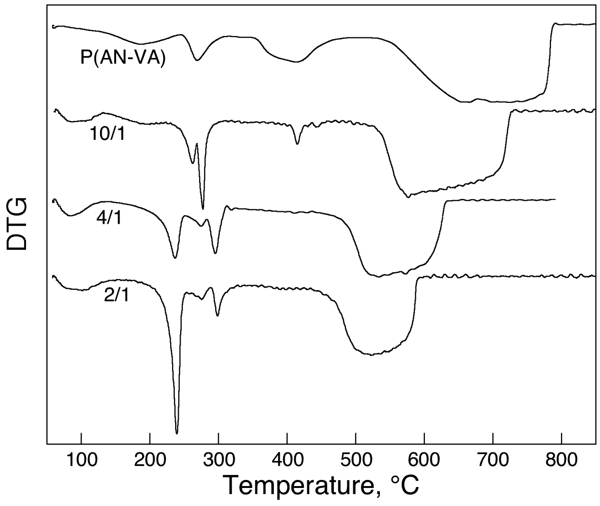

Fig. 10. DTG for P(AN-VA)/YN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

3.3. P(AN-VA)/BaN

3.3.1. Molecular structure

The FTIR spectrum of BaN in Fig. 11 exhibits the same NO_3 bands as the other nitrates (1359, 810 and 732 cm^{-1}) [12,13]. The spectrum for 2/1(BaN) exhibits bands typical of P(AN-VA), NO_3 and residual DMF. The NO_3 band for 2/1(BaN) is at 1359 cm^{-1} and the lack of band splitting indicates that there is no NO_3 ion complex formation. P(AN-VA)/CuN and P(AN-VA)/YN did exhibit the NO_3 band splitting indicative of complex formation. The effects of BaN content on the FTIR spectra is similar to those seen

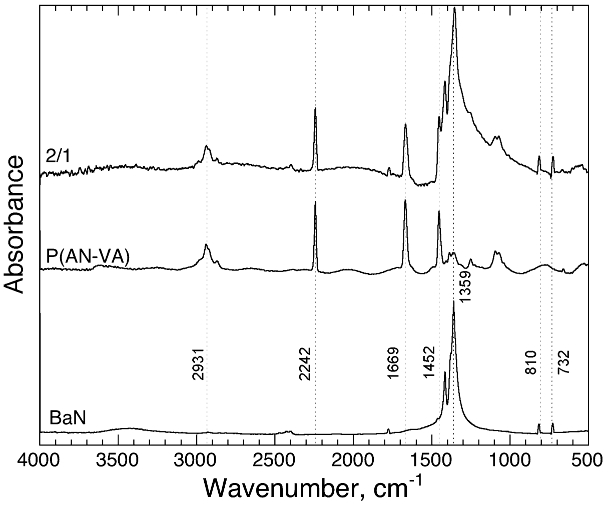

Fig. 11. FTIR spectra of P(AN-VA) as-cast, BaN as-received and 2/1(BaN) as-cast.

for YN and CuN. The relative intensity of C≡N is unaffected by BaN content while the relative intensities of the bands associated with NO_3 increase with BaN content (Fig. 3).

3.3.2. Degradation

The DSC thermograms run in air for P(AN-VA)/BaN are seen in Fig. 12. A summary of the DSC data is presented in Table 3. The exothermic cyclization peak for P(AN-VA) is significantly smaller than the single exothermic peak in P(AN-VA)/BaN at a lower temperature than the cyclization temperature. Reaction 1-BaN, at about 278 °C, has a heat of about 840 $J/g_{P(AN\text{-}VA)}$. This heat is greater than the 690 $J/g_{P(AN\text{-}VA)}$ for P(AN-VA) cyclization at 289 °C. Insight into Reaction 1-BaN is obtained from the FTIR spectra for P(AN-VA) and 2/1(BaN) after exposure to elevated temperatures in Fig. 13. The most significant change in 2/1(BaN) following exposure to 260 °C is the decrease in the NO_3 band at 1359 cm^{-1}. The variations with temperature of the normalized intensities for C≡N and C=N are seen in Fig. 6. The rate of decrease in C≡N is larger than that for P(AN-VA)/YN and is similar to that for P(AN-VA)/CuN. The rate of increase in C=N is similar to that of P(AN-VA)/YN. As seen for the other nitrates, exposing 2/1(BaN) to 325 °C eliminates most of the C≡N but yields significantly less C=N than results from P(AN-VA) cyclization. Reaction 1-BaN is, therefore, a degradation reaction involving the nitrile groups that disrupts cyclization and is similar to Reactions CuN-1 and YN-1. BaN at low concentrations has a more significant effect on the amount of C≡N and C=N at 325 °C than low concentrations of CuN (Fig. 7). Reaction 1-BaN thus involves the nitrile groups but does not produce C=N.

The DTA, TGA and DTG thermograms for P(AN-VA)/BaN are seen in Figs. 14–16, respectively. A summary of the DTA, TGA and DTG data is presented in Table 3.

Table 3
P(AN-VA)/BaN data from the DSC, DTA, TGA and DTG thermograms in air

	P(AN-VA)	P(AN-VA)/BaN		
		10/1	4/1	2/1
	Evaporation	Evaporation		
DTG peak (°C)	185	185	185	185
Mass loss (%)	5.5	3.0	3.0	3.0
	Cyclization	Reaction 1-BaN		
DSC peak (°C)	289	277	279	277
Heat (J/g_{sample})	690	764	663	559
Heat ($J/g_{P(AN\text{-}VA)}$)	690	840	829	839
DTA peak (°C)	263	270	277	284
DTG peak (°C)	270	263	270	273
Mass loss (%)	5.6	18.6	25.8	34.0
Mass loss (g/g_{NO_3})	–	4.31	2.72	2.15
	Carbonization I			
DTA peak (°C)	459	–	–	–
DTG peak (°C)	414	–	–	–
Mass loss (%)	15	–	–	–
	Oxidation	Reaction 2-BaN		
DTA peak (°C)	767	700	582	547
DTG peak (°C)	712	620	563	543
Mass loss (%)	65.0	63.6	49.8	35.5
Mass loss ($g/g_{P(AN\text{-}VA)}$)	0.65	0.70	0.62	0.53
	850 °C	850 °C		
Residual mass (%)	0.7	6.7	14.7	23.9
Residual mass (g/g_{BN})	–	0.74	0.74	0.72

Evaporation of residual DMF produces a DTG peak at 185 °C. The DTA and DTG peaks for Reaction 1-BaN are in good agreement with the DSC peaks (with the differences reflecting the differences in heating rates and techniques).

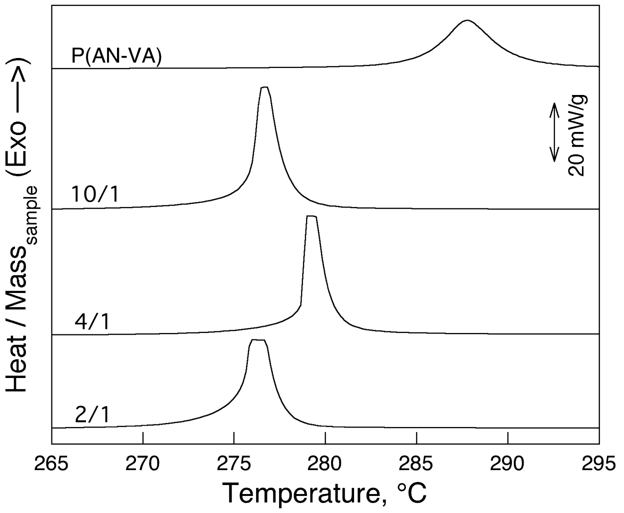

Fig. 12. DSC thermograms for P(AN-VA)/BaN performed from 25 to 350 °C at 10 °C/min in air.

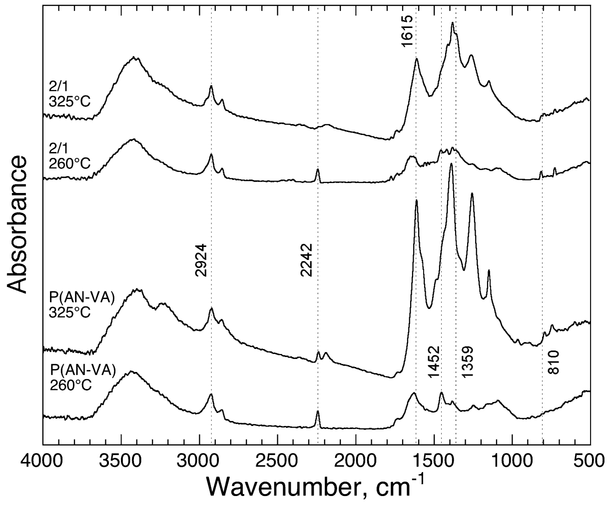

Fig. 13. FTIR spectra of P(AN-VA) and 2/1(BaN) after exposure to either 260 or 325 °C.

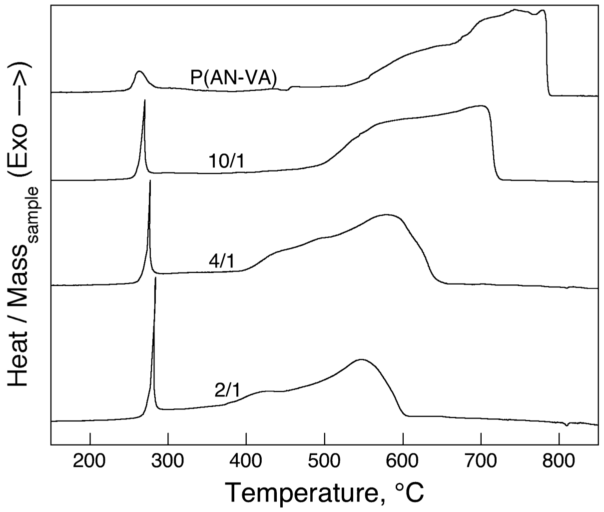

Fig. 14. DTA thermograms for P(AN-VA)/BaN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

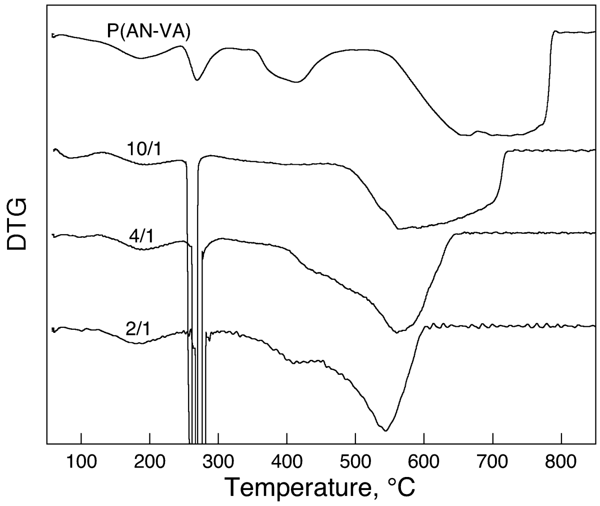

Fig. 16. DTG for P(AN-VA)/BaN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

Reaction 1-BaN produces a significant mass loss; the mass loss for 10/1(BaN) is more than three times that associated with P(AN-VA) cyclization. The mass loss for Reaction 1-BaN is more than twice the NO_3 content and, therefore, must involve P(AN-VA) degradation. Unlike 10/1(CuN) and 10/1(YN), there is no evidence of Carbonization I for 10/1(BaN).

Reaction 2-BaN is largely polymer thermo-oxidative degradation with a mass loss of about 0.62 $g/g_{P(AN\text{-}VA)}$, similar to those of P(AN-VA), P(AN-VA)/CuN and P(AN-VA)/YN. Reaction 2-BaN's initiation temperature, peak temperature and peak width all decrease with BaN content. Reaction 2-BaN for 2/1(BaN), from 350 to 600 °C, has a peak at about 545 °C, significantly lower than that for P(AN-VA). P(AN-VA) degradation is significantly accelerated by the addition of a metal nitrate.

The pyrolysis of P(AN-VA)/BaN can yield BaO, $BaCO_3$ or a combination of both. A calculation assuming the pyrolysis yields BaO predicts a residual mass of 0.59 g/g_{BaN}. A calculation assuming the pyrolysis yields $BaCO_3$ predicts a residual mass of 0.76 g/g_{BaN}. The experimental residual mass of about 0.73 g/g_{BaN} in Table 3 indicates that the product of P(AN-VA)/BaN pyrolysis is largely, if not completely, $BaCO_3$. This result stands in sharp contrast with the production of oxides from CuN and YN. The production of $BaCO_3$ is likely to impede the formation of YBCO [7]. The environments, temperatures, and heating rates in the HTSC precursor pyrolysis process should be chosen to minimize carbonate formation.

The similarities and differences in the effects that CuN, YN and BaN have on P(AN-VA) can be seen in the TGA curves for the 2/1 compositions (Fig. 17). All three nitrates reduce the thermal stability, with CuN producing the most significant decrease. For CuN, there is a 30% mass loss by 170 °C and degradation is complete at about 550 °C. The relatively large effect of CuN may be related to copper's ability to catalyze nitrile reactions [10,17]. Degradation

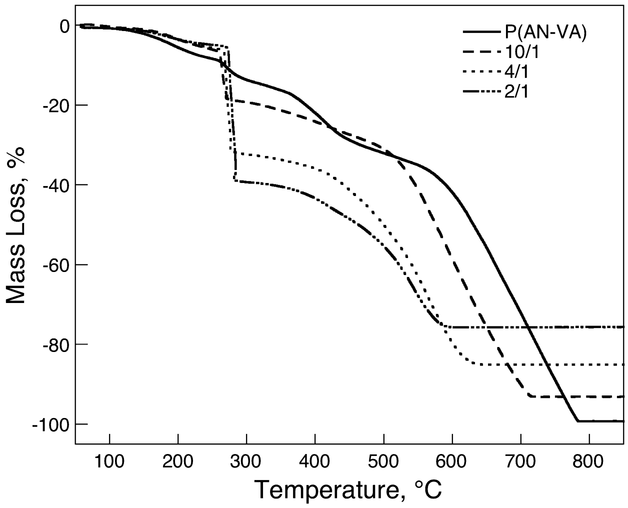

Fig. 15. TGA for P(AN-VA)/BaN performed from 25 °C to beyond 800 °C at 5 °C/min in air.

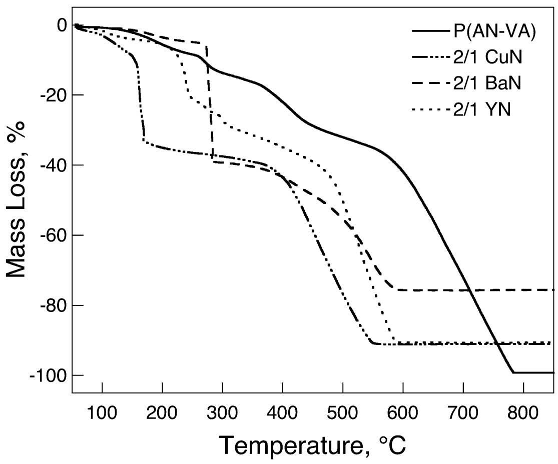

Fig. 17. TGA for P(AN-VA) and 2/1(YN, BaN or CuN) performed from 25 °C to beyond 800 °C at 5 °C/min in air.

begins at somewhat higher temperatures for YN and BaN and is complete by about 600 °C. The effects of CuN and YN on P(AN-VA) degradation seem to correspond with the behavior of the neat nitrates in Fig. 1 and, in both cases, pyrolysis yielded oxides. In spite of the relative stability of neat BaN in Fig. 1, it also accelerated P(AN-VA) degradation (Fig. 17) and disrupted cyclization. BaN is also exceptional in that pyrolysis of neat BaN yielded an oxide while the pyrolysis of P(AN-VA)/BaN yielded a carbonate.

3.4. HTSC formation

Pyrolysis of the HTSC precursor (P(AN-VA)/(Y,Ba,-Cu)N in a 2/1 ratio with Y:Ba:Cu = 1:2:3) was optimized for YBCO production using the process times, temperatures and environments described above. The XRD results in Fig. 18 indicate that YBCO is indeed the dominant phase, although CuO and $BaCuO_2$ contaminant phases are also present. The amount of CuO and $BaCuO_2$ is smaller for the powder than for the film and this may reflect the greater surface area in the powder which would enhance diffusion in and out of the precursor during pyrolysis. The dependence of the final structure on the nature of the polymer can be seen from the fact that an HTSC precursor based on novolac processed under identical conditions did not contain such contaminant phases [19].

4. Conclusions

Yttrium nitrate and barium nitrate had significant effects on P(AN-VA) pyrolysis, disrupting cyclization and reducing the degradation temperature by about 200 °C. These effects, however, were not always predictable from the degradation of the neat nitrate. Pyrolysis of the HTSC precursor successfully yielded a material in which the YBCO phase was dominant.

- For P(AN-VA)/YN, a complex was formed between P(AN-VA) and the NO_3 ion, but there was no evidence of P(AN-VA) coordination with the metal ion. For P(AN-VA)/BaN, there was no evidence of complex formation.
- Pyrolysis of P(AN-VA)/YN and P(AN-VA)/BaN is, in many respects, similar to that of P(AN-VA)/CuN.
- P(AN-VA)/YN exhibited an exotherm at about 244 °C related to the degradation of YN and characterized by a heat of 3400 J/g_{NO_3} (210 kJ/mol_{NO_3}) and a mass loss of 0.90 g/g_{NO_3}. This degradation includes a reaction with the nitrile groups that disrupts the exothermic cyclization reaction at about 286 °C. P(AN-VA)/BaN exhibited a relatively large exotherm at about 278 °C which involves polymer degradation since the associated mass loss was significantly larger than the NO_3 content. The degradation of both BaN and the polymer at about 278 °C prevented cyclization.
- The multi-stage degradation of YN was reflected in the degradation of P(AN-VA)/YN.
- Thermo-oxidative degradation in P(AN-VA)/YN and P(AN-VA)/BaN produced mass losses of 0.65 and 0.62 $g/g_{P(AN\text{-}VA)}$, respectively, similar to that in P(AN-VA).
- 2/1(YN) and 2/1(BaN) reached constant residual masses at about 590 °C, compared to 785 °C for P(AN-VA).
- The pyrolysis of P(AN-VA)/YN yielded Y_2O_3, while that of P(AN-VA)/BaN yielded largely $BaCO_3$.
- The accelerated degradation in P(AN-VA)/BaN and the formation of $BaCO_3$ could not be predicted from the degradation of neat BaN.
- The amount of contaminant phases in the resulting YBCO depended on the form of the HTSC precursor (film or powder) and on the nature of the polymer (P(AN-VA) or novolac).

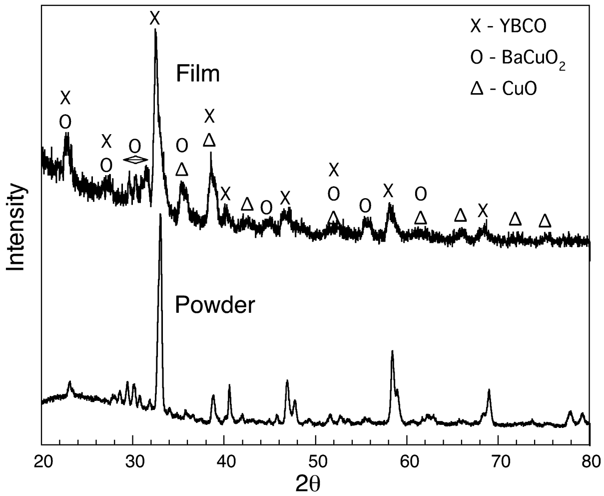

Fig. 18. XRD of HTSC powder and HTSC film cast on $SrTiO_3$ following the multistage pyrolysis process previously described.

Acknowledgements

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