# PREPARATION AND THERMOANALYTIC STUDIES OF YTTRIUM POLY(ACRYLATE)

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A new process for the production of advanced ceramic powders has been studied. The process involves the chelation of a metal ion in solution by an organic acid polymer. Using FTIR, TG, DTG and DTA, the process for the formation of the organo-metallic complex and the decomposition to the metal oxide is reported. Effects of packing density on DTA are also discussed.

Thermal degradation of polymers has been widely studied [1–3]. Recently, thermal degradation of polymers in ceramic particulate systems, in this case the polymer is acting as a binder, have also been investigated [4–6]. This paper will focus on the thermal analysis of a polymer-metal powder, which decomposes to the metal oxide ceramic powder. These metal oxide ceramic powders are of interest due to the properties they have and the relation of these properties to processing of ceramic pieces.

Ceramists strive to produce fine, uniform particles that can be shaped into high prefired density bodies which will sinter to high density. There are several ways to produce these powders, including freeze-drying, sol-gel synthesis, and decomposition of metallo-organics [7]. Each of these methods have disadvantages associated with them. Freeze drying is limited in that it is only applicable to a small number of systems. Sol-gel synthesis is very useful in glassmaking, but it limited in forming ceramic oxides due to high shrinkages (50 + %). Metallo-organic synthesis usually requires using metal alkoxides and therefore the process involves handling volatile and sometimes toxic materials, and preparation in an anhydrous atmosphere [8].

Micheli [9] describes a novel new metallo-organic method of producing sinterable ceramic oxides. His method differs from traditional metallo-organic synthesis in that the reactants are water-soluble metal salts and an organic acid. By using this method the need for an anhydrous system is eliminated and the toxicity is

decreased. To distinguish this method from the traditional method we will refer to it as an organo-metallic method.

Organo-metallic preparation was used to produce several different yttrium polyacrylate powders. Infrared spectroscopy was used to determine the bonding type and chelation degree of the starting powders. The thermal decomposition was studied for each using thermal gravimetric analysis and differential thermal analysis in air. X-ray powder diffration confirmed the decomposition to the oxide.

## Experimental procedures

In a 400 ml beaker, 20,000g of yttrium nitrate hexahydrate, $Y(NO_3)_3 \cdot 6H_2O$[1], were dissolved in 20 ml of distilled water. The pH was determined to be 0.75 using a Hach One pH meter[2]. In a separate beaker, 22.834 g of a 50% stock solution of Good-rite K-732 polyacrylic acid[3] were diluted by mixing with 22 ml of distilled water. The pH was determined to be 2.98. these weights result in an equivalent ratio of yttrium to carboxyl groups of 1:3. This is required to allow for complete octahedral chelation of the trivalent yttrium by the monovalent carboxyl. The polyacrylic acid used in this experiment had a weight-average molecular weight of 5100. The organic acid solution was added to the yttrium solution. The combined solutions had a pH of 1.44. Concentrated ammonium hydroxide was added

Table 1 Precipitation pH and thermal characteristics based on DTA intercept curves. $T_s$ obtained from DTG traces

| pH | Primary exotherm, °C | | | | Loss, wt.%* |
|---|---|---|---|---|---|
| | initiation | $T_s$ | completion | $\Delta T$ | |
| 2.57 | 295 | 335 | 420 | 125 | 75 |
| 2.86 | 295 | 335 | 414 | 119 | 73 |
| 3.25 | 309 | 342 | 414 | 105 | 71 |
| 4.00 | 319 | 354 | 414 | 95 | 69 |
| 4.70 | 324 | 362 | 414 | 90 | 68 |
| 6.05 | 343 | 365 | 410 | 67 | 65 |
| 6.79 | 345 | 372 | 410 | 65 | 62 |
| 7.60 | 345 | 370 | 410 | 65 | 61 |
| 8.00 | 345 | 372 | 412 | 67 | 63 |

* Theoretical weight loss for complete chelation is 63%.

[1] Alfa Chemical Corp., Danvers, MA lot B11G.
[2] Hach Co., Loveland, CO.
[3] BF Goodrich Co., Clev., OH, lot 2603232.

dropwise while the solution was being stirred. Upon addition a white gelatinous precipitate formed. At the pH values listed in Table 1 a small amount of the sample was removed. These samples were washed using distilled water, and vacuum filtered with number 2 filter paper. Each sample was then dried at 110° for 24 hours.

The nature of the bonding and chelation in the precipitates was investigated on the basis of the FTIR spectra obtained with a Nicolet 60 SXR spectrometer[4]. The KBr pellet method was employed, using 1.5 mg of sample in 300 mg of KBr. Spectra were obtained with a resolution of 4 cm$^{-1}$ resulting from 32 scans.

TG and DTA were performed using platinum crucibles and heating rates of 2 deg/min from room temperature to 600°. The sample size was $\approx 10$ mg and the atmosphere was flowing air in both cases. The TG change in weight was monitored using a Cahn 2000 balance[5] while temperature was measured using type S thermocouples. The DTA[6] temperature was measured using type K. An alumina reference, also in a platinum crucible, was used in DTA.

## Results and discussion

The infrared absorption of four of the powders as a function of pH is shown in Fig. 1. The band at 1710 cm$^{-1}$ can be assigned to the C=O vibration of a protonated carboxyl group [10]. As can be seen, as the pH increased, the intensity of the 1710 cm$^{-1}$ band decreases. As the pH is increased, the amount of COOH sites that have dissociated to COO$^-$ increases. When the acid group no longer contains a hydrogen, the 1710 cm$^{-1}$ band will disappear. As each site dissociates it becomes available for chelation to a Y$^{+3}$. The remaining shoulder that can be seen at high pH is due to the length of the polymer chain. Even though the equivalent ratio of yttrium to carboxyl used would allow for complete chelation, based on the length of the polymer chain and the steric effects that would be required to bond each Y$^{+3}$ to three COO$^-$, complete chelation is not achievable. The addition of excess chelating agent could possibly lead to complete chelation, however, this would cause there to be unchelated, or protonated, carboxyl groups which would complicate the thermal decomposition.

By examining the shift in the bands at 1560 cm$^{-1}$ and 1415 cm$^{-1}$ it is possible to determine the coordination of the metal ion to the carboxylate ion, as shown by Nakomoto [11]. In this case, the yttrium was determined to be in a octahedral coordination with each ligand bidentate. The reaction to produce the precipitate is
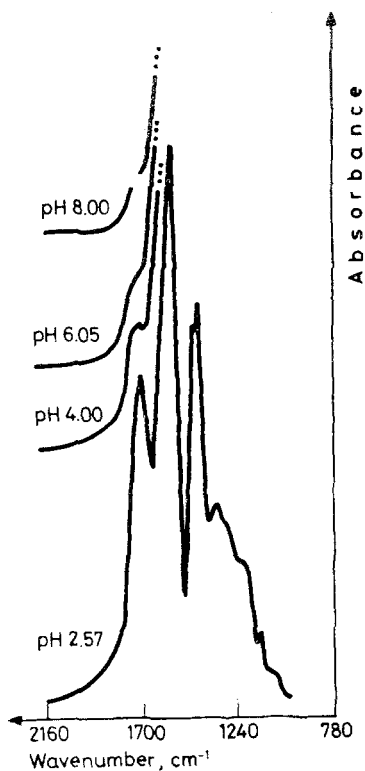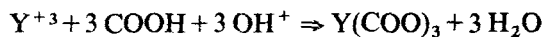
**Fig. 1** Infrared spectra of the yttrium polyacrylate powders showing the decrease in the COOH band (1710 cm$^{-1}$) with increasing precipitation pH

believed to be:

$$Y^{+3} + 3\,COOH + 3\,OH^+ \Rightarrow Y(COO)_3 + 3\,H_2O$$

Thermal gravimetric analyses versus pH are shown in Fig. 2. By taking the first derivative of the TG data with respect to temperature, the temperature of maximum non-isothermal weight loss, $T_s$, could be determined. It can be seen in both Fig. 2 and Table 1 that as the pH at precipitation increase, $T_s$ increases and the width of the DTG plot decreases. Both of these observations describe a situation of increasing activation energy of decomposition as the preparation pH increases [1]. Activation energies could not be determined by Horowitz and Metzger's [12] method as the TG traces were verticle at high pH.

The weight loss from TG is accompanied by a large exotherm as seen in the DTA data presented in Fig. 3. At low precipitation pH there is a very broad primary exotherm and a small secondary exotherm at higher temperatures. As the pH of

precipitation is increased the primary peak increases in temperature and becomes sharper (shown as $\Delta T$ in Table 1) and the secondary exotherm disappears. Table 1 shows that for all except the lowest pH, the completion temperature is approximately 412°, indicating that the broadening of the DTA primary peak is due to a change in initiation temperature, not a shift in completion temperature. The position of the primary peak corresponds very well with the DTG data, as expected.

As pointed out earlier, as the pH is increased the activation energy is increased. This means that the energy required to decompose the material is increased. This would be expected for a high pH tri-chelated material as opposed to the low pH polymer : chelate mixtures. In the low pH materials we have seen two exotherms in
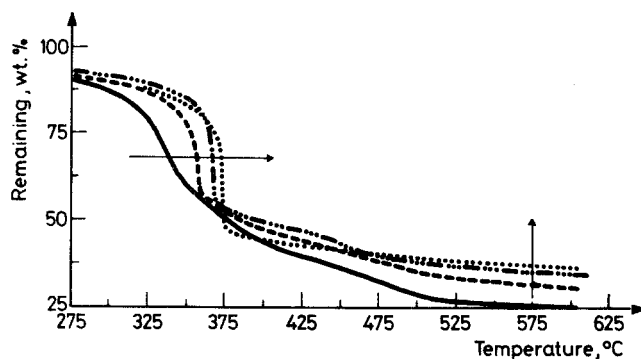


Fig. 2  Effect of precipitation pH on TG trace for yttrium polyacrylate. Note the shift in both $T_s$ and final weight percent remaining with increasing pH. ——— 2.57, – – – 4.00, —·–·— 6.05, ····· 8.00 2 deg/min, flowing air
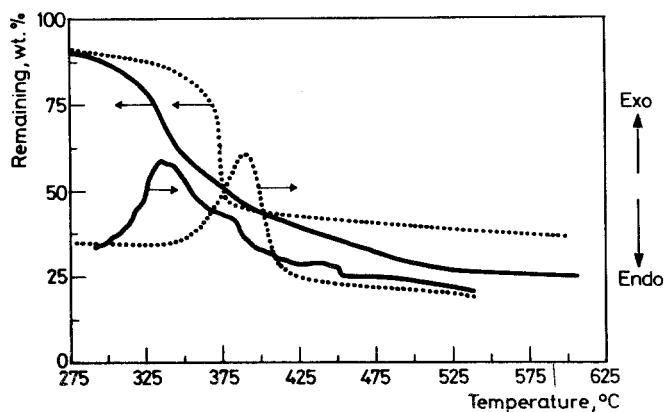


Fig. 3  TG and DTA for the low and high pH powders examined. ——— 2.57, ···· 8.00. 2 deg/min, flowing air

the DTA data. The first, we suspect, is due to the burning of the un-chelated polymer, leaving a carbonaceous ash. This exotherm provides enough energy to activate the decomposition of the yttrium polyacrylate, which has a completion temperature of approximately 412°. The second exotherm that is seen is the burning of the carbonaceous ash. At high pH, there is very little unchelated carboxyl, therefore the $T_s$ value is increased, corresponding to the decomposition of the chelated material, and there is no second exotherm present. The exotherm for the unchelated material decomposition is not observed because of the relatively small amount present. The presence of a small amount of unchelated material may cause the low temperature onset seen for the high pH materials.

It was determined that the sample size used for the DTA played a significant part in the trace that was obtained. Using the powder that was precipitated at a pH of 8.00, several different DTA scans were collected. Each was collected at a heating rate of 2 deg/min in flowing air. Sample weights of 80, 100, and 120 mg each were packed into the same volume. The data collected is shown in Fig. 4, which includes the 10 mg sample from the initial data. As can be seen, as the packing density of the powder increases, the number of exotherms goes from one to three. Also, the temperature where the baseline returns is also increased. Since similar effects of sample size on TG traces would be assumed, sample sizes were kept constant for each measurement.

Assuming a complete chelation of the yttrium and the carboxyl groups, the theoretical weight loss was calculated to be 63%. Table 1 shows the weight loss
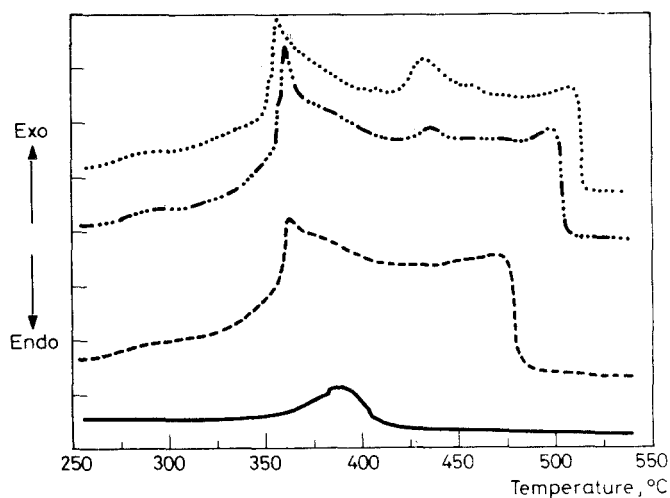


**Fig. 4** Effect of sample size on DTA traces of the powder prepared at pH = 8.00. Baseline shifted for clarity. —— 10 mg, – – – 80 mg, —··— 100 mg, ···· 120 mg. 2 deg/min, flowing air

obtained for the powders as a function of pH. It can be seen that for the powders prepared at the three highest pH values there was approximately theoretical weight loss indicating that there was nearly total chelation. This is also indicated by the FTIR analysis. Of course, as stated earlier, there probably was not complete chelation. However, substituting another anion, such as $OH^-$, onto the yttrium ion would not change the weight loss significantly from the theoretical because the entire polymer chain would still be present, and is the main contributor to the weight loss. At low pH precipitation, there are very few ionized carboxyl groups available for yttrium chelation and therefore a great deal of carboxyl groups contain hydrogen. Since the entire group would then decompose to gaseous products, the weight loss would be greater than theoretical.

The powders as precipitated were X-ray amorphous. However, after heat treatment to 600° the only phase present was $Y_2O_3$. From peak broadening methods the particles were determined to have diameters on the order of 200 Å.

**Conclusions**

Our work has shown that it is possible to reach a state of maximum chelation depending on the pH value of the solution at the time of precipitation. By altering the pH at precipitation it is possible to control the thermal degradation temperatures and rates. This information will be useful in the production of mixed oxide systems by this method. By using infrared spectroscopy and thermal analysis it is possible to approximate the amount of chelation and determine the type of chelation.

It must be recognized that the sample packing density plays a major role in determining the DTA or TG curves of organo-metallic precursors in flowing air. By keeping the sample size similar the results obtained correlate very well with the TG data.

Ceramic oxide powders can be produced by this method at relatively low temperatures, thereby keeping a fine grain size, making them highly desirable for sintering. Our future work will focus on the thermal degradation of other oxide powders produced by this technique as well as the characterization and sintering of these oxide powders.

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**Zusammenfassung** — Ein neues Verfahren zur Herstellung von Keramikpulvern wurde untersucht. Das Verfahren beinhaltet die Chelatisierung eines in Lösung befindlichen Metallions mittels einer polymeren organischen Säure. Unter Zuhilfenahme von FTIR, TG, DTG und DTA wurde der Vorgang der organometallischen Komplexbildung und der zersetzung zu Metalloxid beschrieben. Der Einfluss der Packungsdichte auf die DTA wird ebenfalls beschrieben.

**Резюме** — Изучен новый процесс получения улучшенных керамических порошков, который включает хелатирование в растворе иона металла каким-либо органическим кислотным полимером. Используя фурье-ИК спектроскопию, ТГ, ДТГ и ДТА, изучен прс цесс образования органо-металлического комплекса и разложение его до оксида металла. Обсуждено также влияние плотности набивки на ДТА измерения.