ADVANCES IN ANHYDRIDE EPOXY SYSTEMS

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ABSTRACT

In light of the recent development of tri and tetra-functional epoxy resins, we began to investigate the effectiveness of anhydrides as curing agents for these resins. As our work progressed, certain properties that make these systems well suited for prepreg manufacturer, filament winding and pultrusion were revealed.

The effect of stoichiometry, catalyst, cure schedule as well as resin and anhydride selection are described. Properties studied include the glass transition temperature, room temperature stability, tensile strength, percent elongation, modulas of elasticity, and shrinkage during cure. Wet strength properties of these systems are also described.

INTRODUCTION

The use of anhydrides as curing agents for polyfunctional epoxy resins have not received as much attention as have aromatic diamines, aliphatic diamines and polyamides. In light of the recent advances in the development of polyfunctional epoxy resins, Anhydrides and Chemicals Inc. initiated what is, to our knowledge, the first comprehensive study of commercially important physical properties of anhydride cured polyfunctional epoxy resin systems. Resins were chosen from each of the leading manufacturers on the basis of ease of use and availability. Likewise, a variety of anhydrides were selected including aromatic dianhydrides, mono-anhydrides and polyanhydrides. Common accelerators such as tertiary amines, imidazoles and organo metallic compounds were also used. A preliminary screening for ease of casting was performed since cast sheets were required for physical testing. Once the results were determined, a program for the evaluation of pot life, cure characteristics, mechanical properties and wet strength was initiated.

We hope to use the data from these experiments to assess the suitability of these systems for composites, prepreg and filament winding.

Discussion

In recent years there have been advances in the development of multifunctional epoxy resins. Advantages to the use of these resins include high glass transistion temperatures, high decomposition temperatures, long term high temperature performance and good wet strength performance. The objective of this paper is to evaluate the performance of mono, poly and dianhydrides when employed as curing agents for multifunctional epoxy resins.

The new polyfunctional epoxy resins contain three or four oxirane rings per molecule. Figure 1 contains the structures of the resins included in the study. This equates to a theoretical functionality of six or eight when cured with a mono anhydride which has a functionality of two. According to Carother's theory of condensation polymerzation, any system that contains monomers of three or more functionality reacted with monomers of a two or more functionality will form a crossed linked thermoset product. Here we begin to deal with a monomer of six or eight functionality combined with a monomer of two or four functionality; the latter, as a dianhydride is employed. Therefore, one should expect to achieve a very high crosslink density.

Before I get into the results of our work I would like to briefly review the anhydride-epoxy curing mechanism and discuss what makes the polyfunctional epoxies behave differently than standard bis A epoxy resins.

Standard bis A epoxy-anhydride reactions involve both internal hydroxyl groups and the terminal epoxy groups. The anhydride initially reacts with hydroxyl groups to form half esters (figure 2). Standard bis A epoxies on average contain approximately 0.31 hydroxyl groups per molecule. The half ester with the free carboxyl group is then free to react with an epoxy ring. The reaction with the epoxy results in the creation of another hydroxyl group which can react with another anhydride group, or in the presence of acid groups (free acid) acting as catalysts react with another epoxy group to form an ether linkage (figure 3). This later reaction, although much slower than the ester reaction at elevated temperatures accounts for optimum mix ratios generally being less than the stoichiometric equivalents.

With dianhydrides, pot lives are generally shorter since a high degree of cross linking can occur via reaction between hydroxyl groups only. However, with the polyfunctional epoxies the ratio of epoxy groups to hydroxyl groups is very high (figure 1). And the initial step of the reaction does not readily occur. Therefore, as long as low free acid anhydrides are used, long pot lives can be expected. This is a unique property of anhydride cured systems wherein the highly reactive polyfunctional resins exhibit longer pot lives than many conventional epoxies.

Table 1 shows initial mix viscosities and their room temperature storage life. Tactix 138 was included in this study to contrast a high purity bis A type of epoxy resin with polyfunctional epoxy resins. The room temperature storage life was determined by filling a Gardener Holdt tube up to the appropriate level and measuring the change in viscosity vs. time. Special care was taken to minimize exposure to moist air to prevent the hydrolysis of the anhydride to free acid. The sealed tubes were stored at a constant temperature of 20 degrees C. during the evaluation. Table 1 also shows the effects of stoichiometry on gel time. Here, it is interesting to note that excess anhydride increases room temperature stability.

A significant advantage to the use of liquid anhydrides is their ability to reduce mix viscosity. Many of the polyfunctional epoxy resins are viscous liquids or semisolids. Low viscosity anhydrides (60-300 cps) used in ratios of approximately 1:1 greatly reduced the viscosity of the resin mix and facilitate processing without the use of solvents or other viscosity reducers. Table 2 shows peak exotherms and gel times of some polyfunctional epoxy resins and anhydrides as measured on a DSC. Peak exotherms were determined via a DSC scan from 50 to 200 degrees C. at a rate of 10 degrees C. per minute, and should be used for comparative purposes only. These results also indicate that long working life even at elevated temperatures are characteristic of anhydrides, while fast gel times at elevated temperatures can be easily obtained.

In our study we also looked at the glass transition temperatures of different anhydride epoxy systems. The glass transition temperatures were measured after a cure cycle of one hour at 120 degrees C., two hours at 150 degrees C., and three hours at 200 degrees C. These samples all demonstrated exotherms at or slightly above their glass transition temperatures. Additional cures of 15 and 30 minutes at 300 degrees C. were then performed. The results are summarized in table 3. In this study, the anhydride polyfunctional epoxy systems indicate that glass transition temperatures above the cure temperature are usually achieved. However, due to steric hinderance, even after long cures, DSC scans still reveal that the reaction is incomplete. When additional short cures at 300 degrees C. are applied the Tg is increased and the reaction proceeds towards completion. In this case the increased cure temperature has allowed the system to soften so that additional crosslinking can occur. However, longer exposure i.e. 30 minutes or more at 300 degrees C. temperatures, usually results in a decrease in Tg. This may be the result of either:

1. oxidation or decomposition occurring, or;

2. cracks formed by the significant change in the expansion coefficient as the material passes through the glass transition.

Table 3 also shows the effect of catalyst choice on the Tg. These differences become less significant with longer cures. The slower curing accelerators such as the AC-8 generally provide better casting and are less prone to cracks or internal stress and exhibit better thermal cycling characteristics.

Table 4 shows the result of alternate cures of one hour at 120 degrees C., two hours at 150 degrees C., and twenty one hours at 200 degrees C. Here, Tgs are generally higher than they were after the shorter cure cycle especially when using AC-8 and BDMA as a catalyst. AC-PI seems to have achieved Tg's near the ultimate after only three hours at 200 degrees C. The Tg data indicated that in addition to pot life, the significance of accelerator choice lies in achieving the highest Tg in the shortest amount of time, and is less significant in achieving the ultimate Tg. Perhaps the most crucial element in accelerator choice is in achieving bubble free and crack free castings.

The data in tables 3 and 4 also indicates that stoichiometry of less than one (0.7 in this case) anhydride equivalent per epoxy equivalent gives higher Tgs and short cure cycles, but as cure is lengthened stoichiometry approaching 1:1 yields higher Tgs. Perhaps one explanation of this is that interpenetrating networks are formed wherein the epoxy and anhydride polymerize by a different mechanism once the initial polymer network is formed thereby increasing the Tg.

Table 5 compares the Tg and gel time data of different anhydrides. Here Tg's for AC-32, an aromatic dianhydride, are slightly higher than those of AC-Methyl. Another interesting phenomena observed is that in some systems containing blends of two anhydrides, two distinct exotherms can be observed (figure 4); and frequently, the fully cured resin exhibits two distinct Tgs. After the first Tg there is only a slight change in the slope of the curve while greater change occurs at the second Tg.

Systems were selected for physical testing and checking of our own results at the Polymer Process Institute Of The Stevens Institute Of Technology based on the following criteria:

1. low viscosity

2. ease of workability and de-aeration

3. no stress cracks formed during cure

4. high Tg

Mixtures were then prepared based on 85% stoichiometry. Anhydride A contains a monoanhydride (AC-Methyl), anhydride B contains a polyanhydride flexibilizer (PAPA), anhydride C contains an aromatic dianhydride, AC-32. The resin used was MY 721, and the catalyst chosen was AC-8. Each mixture was poured into a rectangular mold of 5"x 5"x0.125" which was sprayed with dry mold release agent. The molds were placed inside an oven at 120 degrees C. for one hour, then heated to 150 degrees C. for two hours and finally cured at 180 degrees C. for another twenty-one hours. No vacuum was applied.

The plaque sample was cut into small tensile bars (ASTM D638 type V specimen) using a Tensikut machine. The tensile strength and percent elongation at break were obtained using a Tinius Olsen Universal testing machine. The speed used was 0.2 in/min. with a gap separation of 1.0 inch.

Nine flexural specimens were also cut out from the plaque and the flexural strength and modulus of elasticity were obtained using the three point bending fixture, according to ASTM D790 (Method I, Procedure A), with a span of 2 inches. The speed of the flexural test was set at 0.05 in/minute. Six tensile bars and six flexural bar samples of each mixture were soaked in hot distilled water at 180 degrees F. for eight hours. The weight of each specimen was noted before and after the soaking. Three samples from each set were dried and tested immediately for tensile and flexural properties, and the three remaining specimens were tested twenty-four hours later after reconditioning at ambient conditions.

Physical properties of the anhydride cured polyfunctional epoxies are summarized and compared to those of anhydride cured bis A epoxies in Table 6. The polyfunctional resins, as expected, show better high temperature performance and are stiffer with lower elongation. The shrinkage on cure is significantly higher; however, the incorporation of an aromatic dianhydride into the system as is the case with "C" seems to reduce the shrinkage.

The wet strength testing summarized in Tables 7, 8 and 9 show that all of these systems retain most of their physical strength even after the eight hour hot water immersion. Table 7 shows the percentage weight increase. Here all the numbers are significantly less than one percent with the lowest being "C" which contains aromatic dianhydride. Upon reconditioning for twenty-four hours at room temperature, system C shows the greatest tendency to return to its original weight.

Tables 8 and 9 show the effect of immersion on physical properties immediately after immersion and after reconditioning. Here the samples exhibited a decrease in elongation immediately after soaking and a further decrease after reconditioning. However, they all seem to retain most of their original strength properties with sample "C" containing aromatic dianhydride the least effected and sample "B" containing a polyanhydride flexibilizer showing the highest elongation.

Figure 6 shows the results of a typical thermal gravimetric analysis. Here the anhydride cured polyfunctional epoxy shows an onset of decomposition of 353 degrees C. Figure 7 shows the TGA curve for high quality bis A resin cured with the identical anhydride. Here the onset of decomposition occurs at 296 degrees C., 57 degrees C. below the polyfunctional epoxy. Both of these analyses were run in air, not nitrogen.

ADVANTAGES OF ANHYDRIDES

The advantages of using anhydrides rather than aromatic diamines as curing agents for the polyfunctional resins include:

1. anhydrides do not pose the health hazards associated with aromatic diamines.

2. anhydrides and (monoanhydrides) provide greater viscosity reduction without solvents or diluents.

3. anhydride cured systems exhibit, on average, less than half the shrinkage of aromatic diamines during cure.

4. anhydrides especially dianhydrides exhibit excellent wet strength properties.

CONCLUSION

This work opens many questions as to the mechanism and kinetics of the anhydride polyfunctional epoxy reactions. A great deal of work has yet to be done before properties and gel times can be accurately predicted. However, certain potential applications are clearly indicated:

1. The electrical industry is constantly miniaturizing circuitry. Therefore, each component: transformers, resistors, capacitors, silica chips, etc. have to be designed to operate at higher temperatures. The systems indicated herein, we believe, will meet class H, class N, and class R performance. Also due to pot life, low viscosity, and low shrinkage, these systems should be well suited for potting and encapsulation.

2. The multifunctional epoxy resins cured with AC-Methyl have a two-four week pot life at room temperature. At the end of this period the resulting solids remain fusible for an additional one-two months. This indicates the possibility of prepreg manufacture wherein the prepreg will have a room temperature shelf life of two-four weeks. Such prepregs will have Tgs and physical properties well within the ranges of bis-maleimides, and also in the lower ranges of polyimides. Therefore the possibility of low cost epoxy systems effectively competing with bis-maleimides and polyimides is suggested.

In aerospace applications, among others, shear strength of the neat resin at elevated temperatures is a critical factor. Also low moisture absorption and high wet strength retention are critical. These properties are comparatively high-especially when an aromatic dianhydride is used.

3. Many applications for filament wound and pultruded structures are appearing which require high Tgs coupled with good chemical resistance and wet strength. Here again, these systems are indicated.

Table I - Room Temperature Storage

Anhydride % of Stoichiometry	70%		100%		130%	
Resin	Initial Viscosity (Gardner)	RT Storage Life (Days)	Initial Viscosity (Gardner)	RT Storage Life (Days)	Initial Viscosity (Gardner)	RT Storage Life (Days)
Tactix 742	Z-6	21	Z-3	28	Z-1	40
MY 721	Y	14	W	18	U	23
EPI-REZ SU8	>Z6	*				
Tetrad X	W	6	V	10	U	14
Epon 1072	>Z6	*				
Tactix 138	W	13	V	18	X	22

All data based on AC-Methyl Anhydride with 0.1% of an imidazole (AC-PI accellerator)
* These samples turned solid after less than 72 hours at room temperature. However, after one month these samples still melted when heated.

Table II - Room Temperature Storage
Gel Times Via DSC

	Gel Time (Minutes for 60% of Reaction)					Peak
	100°C	130°C	150°C	180°C	200°C	Exotherm Temperature
MY 721	1,600	187	52	6	0.8	186.7
Tactix 742	10,000	800	22	1	0.3	179.2
Tetrad X	170	27	6	2	.7	163.6
EPI-REZ SU8	200	40	18	5	1.6	183
Epon 1072	145	23	8	2	.8	177.2
Tactix 138	900	200	2	.4	.1	181

Formulation: 1. Epoxy equivalent
0.7 Equivalent AC -Methyl Anhydride
0.1 phr AC-PI

Table III A - Effect of Stoichiometry & Accelerator on Tg°C

Resin	Anhydride % of Stoichiometry	AC-PI	AC-8	BDMA
		A	A	A
MY 721	70	245	220	230
	100	245	180	225
	130	170	160	180
Tactix 742	70	235	202	200
	100	230	150	190
	130	220	110	160
EPI-REZ SU8	70	230		
	100	225		
	130	210		
Tetrad X	70	240	165	185
	100	220	160	190
	130	210	140	180
Epon 1072	70	245	210	220
Tactix 138	70	207	185	205
	100	198	150	170
	130	120	110	140

Cure Schedule: A=One Hour at 120°C + two hours at 150°C + three hours at 200°C.

Table III B - Effect of Stoichiometry & Accelerator on Tg°C

Resin	Anhydride % of Stoichiometry	AC-PI	AC-8	BDMA
		B	B	B
MY 721	70	248	250	250
	100	250	240	245
	130	200	200	205
Tactix 742	70	260	215	240
	100	245	180	230
	130	240	170	170
EPI-REZ SU8	70	240		
	100			
	130	220		
Tetrad X	70	250	240	235
	100	250	240	225
	130	220	220	190
Epon 1072	70			
Tactix 138	70	205	195	200
	100	190	190	180
	130	150	140	140

Cure Schedule: B=One Hour at 120°C + two hours at 150°C + three hours at 200°C + fifteen minutes at 300°C.

Table IV - Comparison of Accelerators Tg°C

Resin	Anhydride % of Stoichiometry	AC-PI (0.1 phr)	AC-8 (1.5phr)	BDMA (1.0 phr)
MY 721	70	270	277	273
	100	275	280	280
Tactix 742	70	272	275	270
	100	275	275	275
Tetrad X	70	265	265	270
	100	270	275	275
Epon 1072	70	268	270	265
	100	270	275	270
Tactix 138	70	230	240	235
	100	220	220	210

Cure Schedule: One hour at 120°C + two hours at 150°C + twenty-one hours at 200°C.
All samples used AC-Methyl as the anhydride.

Table V - Anhydride Comparison - Tg°C

	AC-Me	AC-M25	AC-36	MHHPA	AC-32
MY 721	245	255	225	185	260
Tactix 742	235	260	235	190	265
Tetrad X	240	255	225	210	270
Epon 1072	245	250	235	165	
EPI-REZ SU8	230	252	230	185	
Tactix 138	205	220	165	140	215

Formulation: 1 Epoxy Equivalent
0.7 Anhydride Equivalent
0.1 phr AC-PI
Cure Cycle: One hour at 120°C + two hours at 150°C + three hours at 200°C.

TABLE VI
PHYSICAL PROPERTIES

RESIN	TACTIX 138	MY721	MY721	MY721
ANHYDRIDE	A	A	B	C
Tg C	205	275	220	255
% ELONG.	4.8	2.5	3.5	3.1
FLEX. STRENGTH (PSI)	17,500	13,900	9,287	12,025
SHEAR MODULUS 40 C	180,000	181,000	N/T	N/T
150 C	49,000	149,000	N/T	N/T
TENSILE (PSI)	10,700	6,000	4,000	5,100
MODULUS OF ELAST. (PSI)		4.91×10^5	3.97×10^5	4.5×10^5
SHRINKAGE %	1.6	3.2	3.4	2.8

A=AC-METHYL/AC-8 B=AC-METHYL /PAPA/AC8 C=ACM25/AC8
CURE SCHEDULE ONE HOUR AT 120 PLUS TWO HOURS AT 150 PLUS TWENTY ONE HOURS AT 180 C STOICHIOMETRY 0.85

TABLE VII PERCENT WATER UPTAKE AFTER WATER IMMERSION AT 180° F.

SAMPLE	AFTER 8 HRS %	RECONDITIONED 24 HRS %
721/A	0.638 ± 0.016	0.598 ± 0.011
721/B	0.566 ± 0.029	0.516 ± 0.014
721/C	0.131 ± 0.023	0.034 ± 0.022
TACTIX 138/A	1.224 ± 0.034	0.986 ± 0.030

A=AC-METHYL/AC-8 B=AC-METHYL /PAPA/AC8 C=ACM25/AC8
CURE SCHEDULE 1 HR AT 120, PLUS 2 HRS AT 150 PLUS 21 HRS AT 180 C. STOICHIOMETRY 0.85

TABLE VIII PHYSICAL PROPERTIES AFTER IMMERSION AT 180° F. FOR EIGHT HOURS

RESIN	MY721	MY721	MY721
ANHYDRIDE	A	B	C
% ELONG.	2.8	2.9	1.9
TENSILE (PSI)	5,100	3,500	5,300
FLEX. STRENGTH PSI	12,200	6,800	10,500
MODULUS OF ELAST. PSI	4.31×10^5	3.82×10^5	4.22×10^5

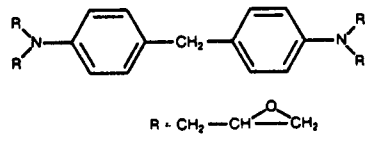
A=AC-METHYL/AC-8 B=AC-METHYL /PAPA/AC8 C=ACM25/AC8
CURE SCHEDULE 1 HR AT 120, PLUS 2 HR AT 150 PLUS 21 HR AT 180 C. STOICHIOMETRY 0.85

TABLE IX PHYSICAL PROPERTIES AFTER RECONDITIONING FOR 24 HOURS

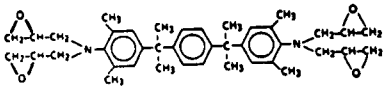
RESIN	MY721	MY721	MY721
ANHYDRIDE	A	B	C
% ELONG.	2.2	2.4	1.8
TENSILE (PSI)	4,600	3,400	5,300
FLEX. STRENGTH PSI	12,200	6,400	12,050
MODULUS OF ELAST. PSI	4.42×10^5	4.57×10^5	4.59×10^5

A=AC-METHYL/AC-8 B=AC-METHYL /PAPA/AC8 C=ACM25/AC8
CURE SCHEDULE 1 HR AT 120, PLUS 2 HR AT 150 PLUS 21 HR AT 180 C. STOICHIOMETRY 0.85

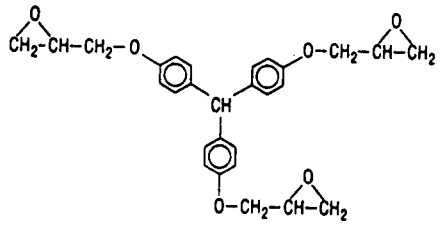
Figure 1



MY 721



EPON 1072



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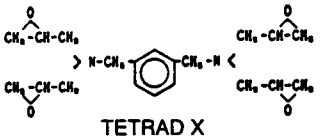
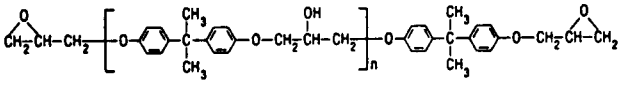


TETRAD X



TACTIX 138

Figure 2

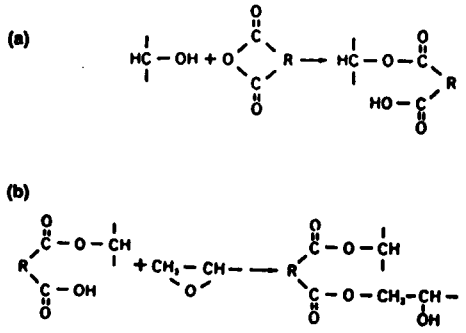


Figure 3

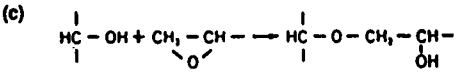


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Figure 4

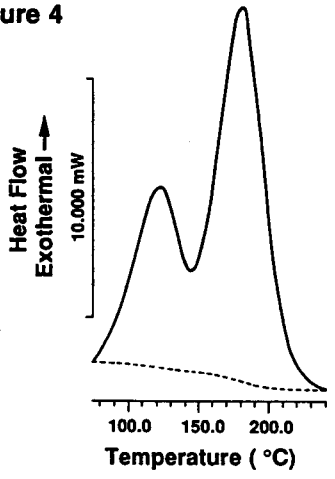

Figure 5

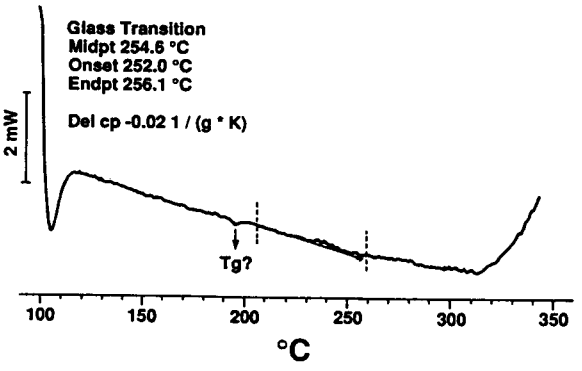

Figure 6

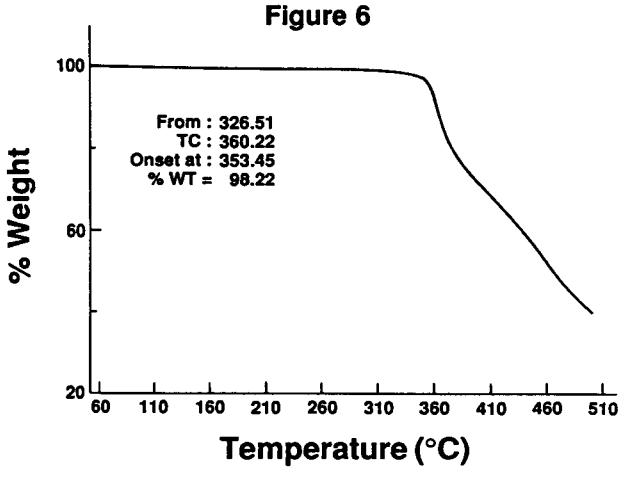
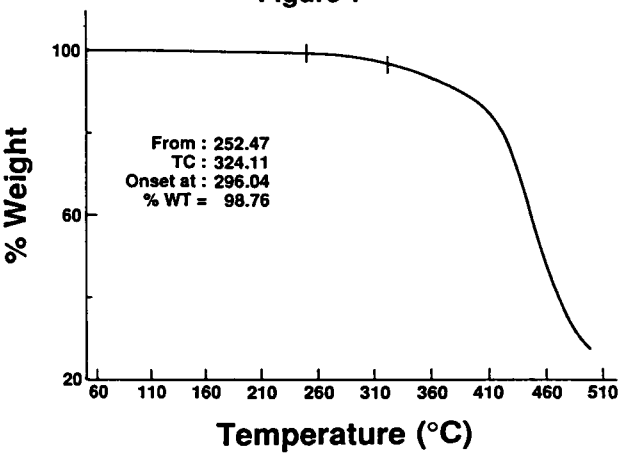
Figure 7