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SYNTHESIS OF IMPROVED POLYESTER RESINS

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SUMMARY

SYNTHESIS OF IMPROVED POLYESTER RESINS

Eighteen aromatic unsaturated polyester prepolymers were synthesized using a modified interfacial condensation reaction. These prepolymers were evaluated for their potential to provide a char forming resin. A total of 27 unsaturated reactive monomers were also screened as a coreactant solvent for the polyester prepolymer.

The best system contained a polyester prepolymer of phthalic, fumaric and diphenic acids reacted with 2,7-naphthalene diol and 9,9-bis(4-hydroxyphenyl)fluorene. This prepolymer was found to be very soluble in several reactive monomers including styrene, divinylbenzene, triallyl cyanurate, diallyl isophthalate and methylvinylpyridine. It provided anaerobic char yields as high as 41 percent at 800^{o}C, and distortion temperature under load (DTUL) as high as 158^{o}C.

This combination of good solubility and char yield represents a significant improvement over state-of-the-art polyester resins.

Composites prepared with the resin (prepolymer with styrene) and Thornel 300 carbon fiber failed to produce acceptable mechanical properties, possibly due to inhibition of the free radical cure and/or lack of wetting of the carbon fibers. It is believed this problem can be overcome by the use of a polyester compatible size on the fiber and/or use of reactive monomers other than styrene with the prepolymer.

SECTION I
INTRODUCTION

BACKGROUND

When graphite fiber/epoxy composites are burned, the graphite fibers burn less rapidly than the matrix resin, and thereby present the potential for free fibers to be swept into the air by the fire. Free graphite fibers have the potential of interfering with the electrical equipment used for communication and for other functions.

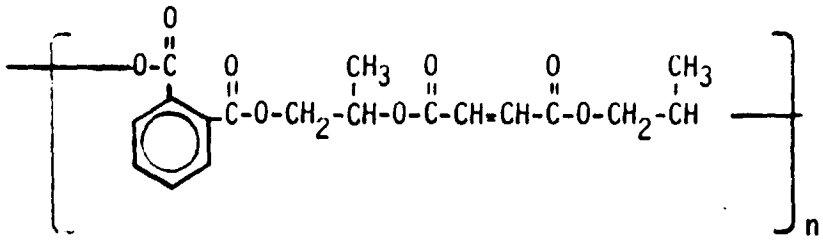
This program was initiated to develop a polyester resin that chars in a fire environment. It is assumed that, if this resin char erodes at about the same rate as the graphite fiber, no fiber will be freed by the fire. Additional requirements are that the resin will be suitable for long term thermooxidative stability in the range of 149 to 177°C (300° to 350°F); the resin should be inexpensive; and must be easily processable into graphite fiber composites.

Polyester resins are logical candidates for this study because of their low cost, good mechanical properties, and excellent processing characteristics. They also have the advantage that it is possible to vary the properties over a wide range by careful selection of the starting materials used in the resin. Unfortunately, available polyester resins are generally unsuitable for high temperature service, and tend to erode rapidly in a fire situation. It is therefore the objective of this program to select the proper starting monomers to overcome these problems, with minimum sacrifice of the excellent processability of polyester resins.

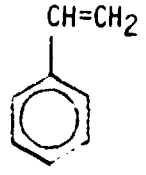
APPROACH

Polyesters are principally divided between saturated and unsaturated products. Saturated polyesters are used typically in films, fibers or cross-linked coatings. Unsaturated polyester resins are of interest to this program since they are used widely as laminating and molding materials.

A typical uncured polyester laminating resin is a linear polyester (alkyd) prepolymer, made from one or more diols and diacids, and dissolved in a reactive solvent. In typical commercial general purpose laminating resins, the diol is propylene glycol; the two diacids are fumaric, (or maleic) acid and phthalic acid (or isophthalic acid); and the reactive monomer is styrene as sketched below.



Polyester Prepolymer (70%)
Mol. Wt. ∿2000



Styrene (30%)

Constituents of a typical polyester laminating resin.

In addition, several additives will be included in the liquid resin including inhibitors, cure control agents, ultraviolet absorbers, etc. The liquid resin is cured by a crosslinking through the unsaturation by a free radical cure. Cure is usually initiated by a free radical source, or alternatively by various types of energy including heat, light or radiation.

The most frequently used cure method is incorporation of an organic peroxide into the resin. This peroxide is frequently called a catalyst but is in fact consumed in the reaction. Since the addition cure process gives

off no volatiles, void free parts result if the monomers do not boil from the reaction exotherm.

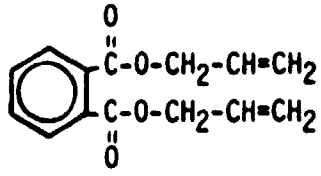
The previously described starting materials are used most frequently since they are among the least expensive of the possible starting materials, and give good overall properties. If better than average properties are required or if there are specific requirements for some improved property (e.g., fire resistance, flexibility, chemical resistance, etc.) many other diols, diacids and reactive monomers can be substituted in whole or in part to give the desired properties. This substitution generally results in an increased cost, and sometimes results in more difficult processing or the partial loss of another desireable property.

It is also possible to modify the properties by changing the quantity of unsaturation in the polyester backbone. Mole ratios of unsaturated to saturated acids generally vary within the range of 1/3 to 3/1 which represents between two and ten unsaturations per molecule. Resins from prepolymers with lower unsaturation ratios tend to be flexible while resins using higher ratio prepolymers are brittle. Balanced resin properties are obtained from prepolymers with unsaturation ratios of 1/1.

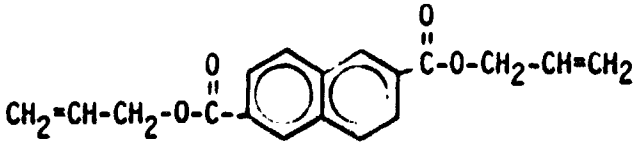
One of the more tedious tasks in the manufacture of polyester backbones is finding ratios of starting materials that will result in the resin being soluble in the reactive monomer. Specifically it has been found that the resin must cure to provide homogeneous and clear products to obtain optimum properties. It is not absolutely required that the polyester backbone be soluble in the monomer at room temperature, however the solution must be complete before final cure. It is known that symmetrical monomers such as ethylene glycol or terephthalic acid cause excessive crystallinity in the backbone polymer. Pendant groups break up the crystalline nature of materials and lower their melting points thereby making them soluble in the reactive monomer.

Another class of polyester resin is based on placing the reactive groups on the ends of the polyester backbone and not within the backbone

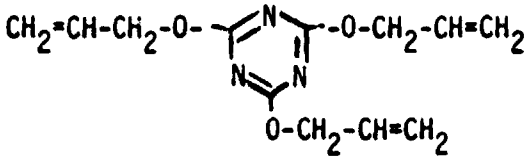
itself. Such end capped backbones can also include unsaturation in the backbone. Examples of this class of polyester resins include diallyl phthalate (DAP), triallyl cyanurate (TAC), diallyl naphthalate (DAN) or acrylate endcaps on epoxy resins (Epocryl as shown below):



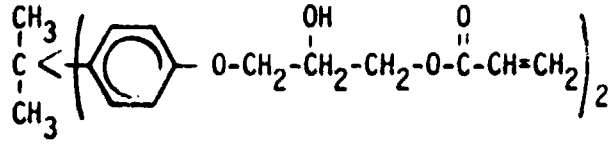
Diallyl Phthalate (DAP)



2,6-Diallyl Naphthalate (DAN)



Triallyl Cyanurate (TAC)



Epocryl (EPON 828 with acrylic acid)

A major difference from the fumaric or maleic acid ester type of polyester is that they can be more difficult to cure and thus require elevated temperature for cure. Since they are "slower" they are most frequently used precatalyzed, in preimpregnated glass fabric or as molding materials.

Within the framework of polyester chemistry and preferred monomers discussed above, several approaches can be taken toward improving the char yield of such systems. The principles discussed below outline our approach to improved char yield polyester resins.

It is known that polyester resins deteriorate under heat principally due to the thermal unzipping of the free radical cured portion of the polymer, and that the polyester backbone is relatively stable thermally. Generally, higher aromatic content backbones provide higher thermal stability. Further

to obtain a high carbon char yield from a polymer, it was assumed that the prepolymer should have a high initial aromatic carbon content. With this in mind, it is necessary to remove the bulk of the alphatic portions of the polyester backbone and replace them with aromatic segments in order to obtain improved heat resistance and the potential for good carbon char. In this regard, the use of phthalic acid is acceptable, however naphthalene or biphenyl dicarboxylic acids were expected to provide higher char yields than phthalic acid. The unsaturated portion of the backbone (e.g., fumaric acid) is required for cure of such backbones and cannot be replaced with aromatic groups. However, the likely place to increase the aromatic content of the polyester backbone is in its diol portion. This could be accomplished with a variety of bisphenols and naphthalene diols, however, such changes reduce the solubility of the polyester backbone in the reactive monomer.

Depolymerization of the free radical cured portion of styrene-modified polyesters occurs readily, liberating styrene monomer. A solution to this problem could be to use reactive monomers that are multifunctional or that contain polar groups, so that under heat, the monomer is not lost as rapidly as styrene. Several obvious choices of the available liquid monomers to replace styrene included divinylbenzene, diallylphthalate, triallylcyanurate, or vinylpyridine.

An alternate approach to optimizing char yield is to add char forming catalysts such as phosphorous compounds. Since phosphate esters can be used in the manufacture of polyester resins, the ideal method to introduce such catalysts may be to incorporate phosphorous into the polymer backbone.

SECTION II
OBJECTIVE

The principal objective of this program was to synthesize and evaluate new polyester resins with improved heat resistance and char-forming properties for use in carbon/graphite fiber composites.

Ancillary objectives included retention of the excellent processability of polyesters and attainment of quality graphite composites.

SECTION III
RESULTS AND DISCUSSION

UNSATURATED POLYESTER PREPOLYMERS

Prepolymer Synthesis and Characterization

A literature survey of recent synthetic methods for aromatic polyester prepolymers and saturated polyester polymers showed that the general method used is an interfacial condensation technique (References 1 through 8). Typically, an aromatic diacid chloride is dissolved in an organic solvent and added with stirring to a bisphenol dissolved in aqueous NaOH containing a small amount of surfactant.

Using this method, Howerton (Reference 6) reported that solutions of unendcapped aromatic polyesters (saturated) degraded or gelled on standing, and that these effects were more severe in solvents that were hydrogen donors such as alcohols. He found that these effects could be prevented by using monofunctional polymer chain terminators (phenols or aromatic acids). He also found that these chain terminators significantly improved the heat resistance of the polymers. Based on this patent, all polyester prepolymers made on this program contained monofunctional endcaps on the prepolymer chain to significantly reduce the residual unreacted phenolic and acid groups.

A preliminary reaction of 2,6-naphthalene dicarboxylic acid chloride with 2,6-naphthalene diol in 1,2-dichloroethane using this method, showed that the polymer quickly became insoluble in the solvent and that the procedure would not be suitable for further endcapping with allyl alcohol.

Aito (Reference 8) reported a commercial polyester resin from 2,6-diallyl naphthalate (DAN) that had appreciably better flexural strength and thermal stability at 260°C than either diallyl phthalate or diallyl isophthalate resins. Unfortunately, communication with Teijim Limited (Japan) revealed that the DAN prepolymer and monomer along with the 2,6-naphthalene dicarboxylic acid were no longer available.

Morgan (Reference 1) reported that chloro-bromo solvents were better solvents for aromatic polyesters than the corresponding dichlorinated solvent. Specifically, he recommends chlorobromethane and 1-chloro-1-bromoethane. Other solvents used by various authors to dissolve aromatic polyesters included m-cresol, sym-tetrachloroethane, phenol, chloroform, 1,2-dichloroethane, tetrahydrofuran, pyridine, 1,1,2-trichloroethane, and dioxane.

The method used exclusively on this program is detailed in a patent by Sokolov and Kudim (Reference 7). These investigators used a modified interfacial condensation method along with added alkali metal salts to obtain yields as high as 99.7 percent of the desired aromatic polyester polymers. This method is also successful for preparation of unsaturated polyester resins. Sokolov and Kudim's modification is to use organic solvents with moderately good solubility in water such as dioxane or tetrahydrofuran (THF).

With this procedure, the inorganic salt (KCl or NaCl) reduces the rate of hydrolysis of the acid chloride, while the increased solubility allows the polymerization to proceed at a high rate.

Nineteen different unsaturated polyester prepolymers were prepared using the method described by Sokolov. Table 1 provides the composition of these prepolymers, their calculated theoretical molecular weights, and the yields obtained from approximately 10 gram (0.005 mole) reactions.

The table shows theoretical molecular weights in the range of 1700 to 2800, which is typical of many commercial polyester prepolymers. It can be

TABLE 1. COMPOSITION (MOLE RATIOS) OF POLYESTER PREPOLYMERS

Code	Diacid Chloride						Diol		Endcap		Theoretical Molecular Weight $\bar{M}_w$	Observed Molecular Weight $\bar{M}_n$	Yield, %
	2,6-Naphthalene	Phthalic	Fumaric	Diphenic	p-Phenylene bis(phenylphosphoric)	Phenylphosphoric	2,7-Naphthalene diol	9,9-bis(4-hydroxyphenyl)fluorene	1-Naphthol	Allyl alcohol			
P1		6					5			2	1696	1135	27
P2	6						5			2	1996		70
P3	2		4				5		2		1768		64
P4	3		3				5		2		1868		67
P5	4		2				5		2		1968		66
P6		3	3				5		2		1720		41, 76
P7		3	3					5	2		2764	1020	54
P8		2	3			1	5		2		1790		26
P9		2.7	3			0.3	5		2		1807		40
P10		2.9	3			0.1	5		2		1812		38
P11			3		≈3		5		2		--		*
P12			3	3			5		2		1948		56
P13		1	3	2			5		2		1872		59
P14		2	3	1			5		2		1796		67
P15		1	3	2			5		2		2822		30
P16		1	3	2			1.5	3.5	2		2531		88(80)
P17		1	3	2			3.5	1.5	2		2151		90
P18		1	3	2			2.5	2.5	2		2341		86
P19	6							5		2	--		Nil-

*Purity questionable

seen that the prepolymers are all reaction products of six mole ratios of diacid chloride with five mole ratios of diphenol, end capped with two mole ratios of 1-naphthol or allyl alcohol. In addition the table shows yields in the range of 26 to 90 percent.

Experimental procedures used to make these prepolymers are discussed in the experiment section of this report.

Most of the prepolymers were endcapped with 1-naphthol. This endcap was selected to increase the char yield and heat resistance of the material, and to reduce the degradation on standing as reported by Howerton.

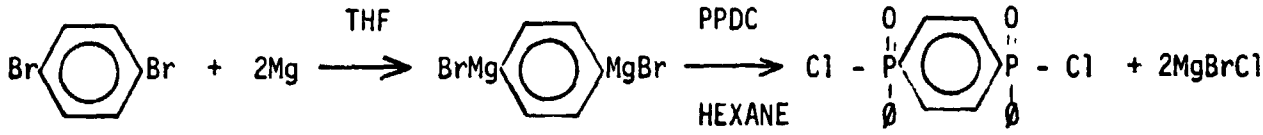
The allyl endcap on the other prepolymers provided the needed unsaturations for crosslinking during the cure cycle. Since allyl alcohol is not as acidic as phenol, it was pre-reacted with the acid chloride prior to the polymerization reaction.

Prepolymers P2 through P5, which were made using the acid chloride of 2,6-naphthalenedicarboxylic and (NDCA), were easier to purify than the other prepolymers as they precipitated as fine powders during reaction workup. In contrast, the other prepolymers tended to be somewhat sticky, especially the prepolymers with high phthalic acid or 9,9-bis(4-hydroxyphenyl)fluorene (BHPF) contents. While these NDCA prepolymers showed better than average char yields, they had melting points above 300^{o}C, and were insoluble in the reactive monomers. Evaluation of NDCA stopped when it was found that the monomer was no longer commercially available.

In contrast to the NDCA prepolymers which precipitate from the prepolymer purification/isolation step as fine powders, prepolymers made with more than two mole ratios of phthalic acid (PA) tended to oil out of solution, thereby making their purification difficult. This problem of oiling out of solution was observed with prepolymer P15 which contained a high mole ratio of 9,9-bis(4-hydroxyphenyl)fluorene (BHPF). Other prepolymers tended to precipate as sticky solids, however, all of the prepolymers were powderable after their final purification.

The fact that some materials did not precipitate as a fine powder indicates that they are not highly crystallized and that they should have greater solubility in the reactive monomers. In order to further reduce the crystallinity and thereby increase the solubility of the prepolymers in the reactive monomers, it is frequently found necessary to have several different diacids and diols in the prepolymer.

Four prepolymers which incorporated different amounts of phosphorus were prepared to determine the effect of this element on the char yield. One prepolymer (P11) was prepared from p-phenylenedi(phenylphosphonyl chloride) (PPPC). The PPPC monomer was made from the p-phenylene bis(magnesium bromide) Grignard reaction with phenylphosphonyl dichloride (PPDC) as shown below.



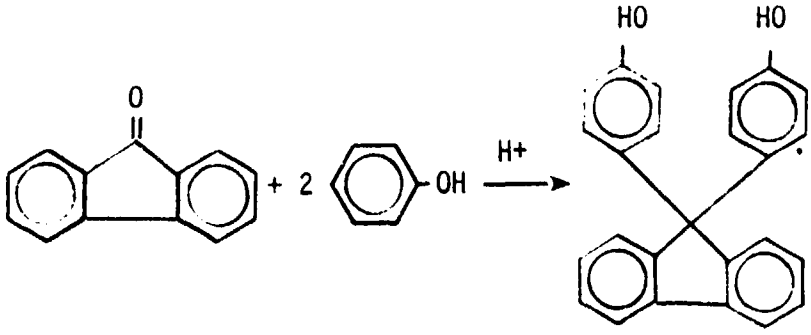
PPPC

The PPPC used in the prepolymer synthesis was contaminated with a small amount of PPDC as indicated by elemental analysis. Further attempts to remove the PPDC by distillation under vacuum caused the product to darken and decompose. It was eventually decided to use the impure PPPC for the synthesis because a small quantity of PPDC should not greatly effect the nature of the prepolymer. The prepolymer recovered from the reaction was a greyish powder which decomposed on vacuum drying at 120^{o}C to a black char-like foam.

The other three phosphorus containing prepolymers (P8 to P10) where 1-naphthol endcapped reaction products of 2,7-naphthalene diol with various ratios of PPDC, phthalic and fumaric acid (chlorides). Elemental analysis of prepolymers P8 and P10 for phosphorus shows that this element was present in approximately 1/3 the theoretical level in both polymers. This suggests that the phosphorus type acid chloride may not work well with the Sokolov procedure.

Polyester prepolymers prepared with BHPF all had generally good solubility and reasonable char yields. The cross-planar nature of the BHPF molecule appears to reduce the crystalline nature of its prepolymers and thereby increase the solubility of such prepolymers in reactive monomers. The highly aromatic nature of the molecule also helps to improve the char yield of its polymer.

The initial lot of BHPF monomer was prepared at Acurex in 90 percent yield (crude) by the method described by Morgan (Reference 1). This synthesis route is sketched below.



Fluorenone Phenol BHPF

This purified diol, and a second lot of BHPF supplied by NASA Ames*, were used to make several prepolymers.

The first prepolymer prepared from the BHPF (allyl endcapped polymer with 2,6-NDCA acid chloride) (P19, Table 1) failed to precipitate from the reaction mixture when excess water was added. Copious quantities of unreacted monomer precipitated, however when the solution was acidified. The reason for the apparent hydrolysis instead of polymerization is not known.

Initial prepolymer preparation using BHPF used the material in an aqueous NaOH·KCl solution in which the BHPF is insoluble at room temperature. Very slight warming causes the compound to go into solution. Using this warmed solution in the Sokolov procedure has resulted in relatively high reaction exotherms, poor yields and low molecular weights. The solubility of the BHPF used to make the later prepolymers (P15 to P18) was improved by adding THF to the H_2O·NaOH·KCl solvent (approximately 40 THF/100 H_2O·NaOH·KCl).

*Courtesy of Dr. John Parker.

With the added THF the BHPF was very soluble at room temperature.

Prepolymer P15 was made by mixing the two solutions of the reactants at room temperature. A significant exotherm resulted, and the prepolymer was recovered in low yield. Prepolymers P16 to P18 were made after the reactants were cooled to well below room temperature. No apparent exotherm was detected (touch) with these reactions, and excellent yields were obtained.

The yield of prepolymer P6 was also increased from 42 percent to 76 percent with the only difference being that the higher yield material was cooled prior to reaction. It therefore seems that cooling of the reaction ingredients prior to mixing is mandatory.

Diphenic acid (biphenyl-2,2'-dicarboxylic acid) was selected for use in prepolymers P12 through P18 because of its aromatic content and its structure. Its structure should reduce prepolymer crystallinity and improve its overall solubility in the reactive monomer.

The combination of diphenic acid with BHPF results in prepolymers which have significantly better solubility than the other prepolymers tested. The combination also produces resins which give excellent char yields for polyester systems. Based on these two important properties, this prepolymer system was selected for the fabrication of carbon fiber reinforced laminates since none of the other prepolymer systems evaluated had demonstrated such potential for success.

The infrared spectrum of this prepolymer (P16) is given in Figure 1.

Molecular weight determination on several prepolymers was attempted. Suitable solvents could not be obtained for prepolymers which contained NDCA. The molecular weights for two prepolymers that were soluble in THF is given in Table 1.

The weight average molecular weight, $\overline{M}_w$ was calculated from the mole ratios of the monomers, while the number average molecular $\overline{M}_n$ was found experimentally by osmometry. The data in Table 1 shows reasonable agreement

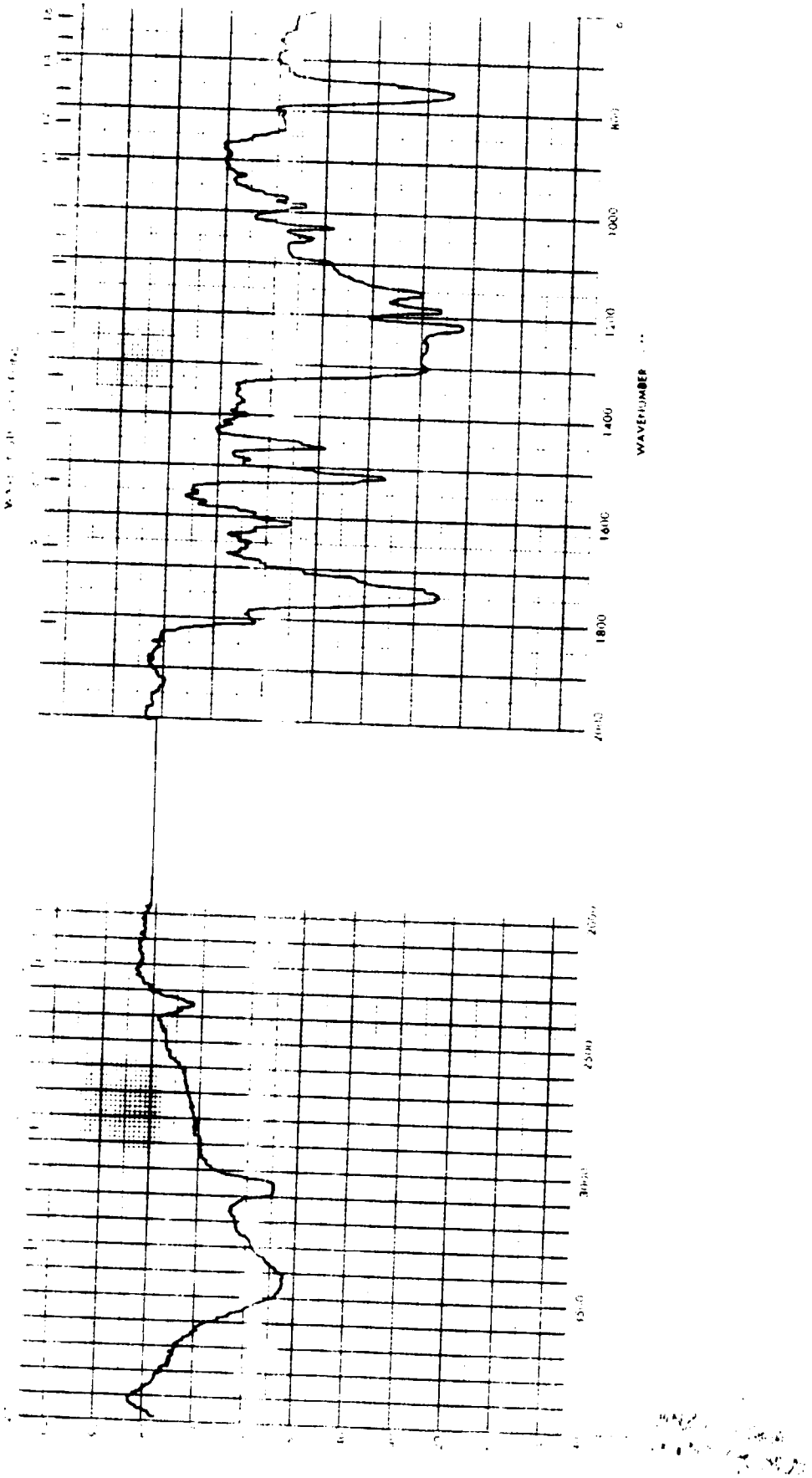


Figure 1. IR spectrum of prepolymer P16.

in the prepolymer molecular weight values, however prepolymer P7 appears to contain low molecular weight fragments or monomers.

The planned analysis for unsaturation was dropped because the methods are not quantitative. A brief review of analytical procedures and conversations with polyester manufacturers indicated unsaturation tests are not normally run on polyester prepolymers since they are only meaningful if similar polymers of known unsaturation are used as standards.

Prepolymer Scaleup

Prepolymer P16 was selected to be used for the matrix material in the carbon fiber reinforced composites.

In order to meet this larger demand for resin, the prepolymer synthesis was scaled-up in two steps. The first scaleup synthesis was to a 100 gram quantity (ten times the previous preparation).

The procedure used was similar to the method used previously in which acid chlorides are reacted with alkaline solutions of phenols in a two phase tetrahydrofuran (THF)/salt water solution.

It is necessary to keep the highly exothermic reaction cooled to obtain good yields. In small scale reactions, external cooling prior to and during the reaction was adequate to control the exotherm. With the 100g preparation, half the water was replaced with ice. It was also necessary to dissolve the 9,9-bis(4-hydroxyphenyl)fluorene in THF as it is almost insoluble in cold alkaline solutions. This procedure is given in the experimental section of this report.

Attempts to further scaleup the synthesis of the polyester prepolymer by a factor of three over the 100 gram scale discussed above resulted in a low yield. The yield obtained was only 34 percent compared to the 87 percent yield obtained from the 100g preparation. The bulk of the reaction mixture appeared to be low molecular weight material which is soluble in alcohol.

Infrared analysis (heat), gel properties and DTULs (styrene comonomer) of resin samples from the 100 and 300 gram prepolymer preparations were essentially equivalent. The prepolymer from the 300 gram preparation is more readily soluble in styrene than the 100g prepolymer. Prepolymer molecular weight distribution in the prepolymer is the likely difference in the two prepolymers however, without further study actual differences in the two prepolymers remain speculative.

UNSATURATED LIQUID MONOMERS

A number of commercially available monomeric vinyl, allyl and methacrylate derivatives were evaluated for their char forming properties. The best materials selected from this study were then cured with polyester prepolymers described previously and again evaluated for their char yields. It was found that the reactive monomers did not contribute to the polymer char yield.

The reactive monomer serves several important functions in a polyester resin. It obviously contributes to the final physical properties of the system, but more important it acts as a solvent for the system, and is required for the free radical cure. Fumaric acid unsaturation does not cure readily under typical polyester cure conditions unless a suitably reactive monomer is available to copolymerize with it.

The unsaturated monomers shown in Table 2 were polymerized in glass vials using 1-gram samples of monomer with 0.01g of mixed organic peroxides as initiator. The peroxides used were benzoyl peroxide, cumene hydroperoxide, t-butyl peroxybenzoate and 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane. They were used as a 10 percent total solids solution in toluene. These peroxides decompose at different temperatures so that cure continues as the samples are heated. The cure cycle used was to heat the samples in 25^{o}C increments between 25^{o}C and 175^{o}C and hold the temperature for 45 minute intervals at each temperature. After cure, the samples were reweighed and placed in a 400^{o}C furnace (air) for one hour and the weight loss determined. The samples were then placed in a 700^{o}C furnace (air) for an additional ten minutes and the weight loss again determined.

TABLE 2. UNSATURATED MONOMERS

	Monomer Properties	Prop. After Cure @175°C	Prop. After Cure @RT	% Residue after 1 hr @400-425°C	After additional 10 min. @700°C: % Residue	Char Strength	Volume of Foam per gram monomer	Foam ρ, g/cc	Q/e Values (Ref. 9): e	Q
1. Styrene	Liquid	Liquid	Solid	0.9	Nil	--	--	--	-0.80	1.000
2. Triallyl cyanurate	Liquid	Solid	Solid	65.7	14.3	Excel.	3.3	0.4	-1.00	0.02
3. Divinylbenzene	Liquid	Solid	Foam(Solid)	32.9(59)	23.6(22)	Excel.	1.8	0.13	-1.77	3.35
4. 2-Vinylnaphthalene	Solid	Liquid	Solid	29.2	19.2	V. Good	3.5	0.05	-0.38	1.25
5. 4-Vinylbiphenyl	Solid	Liquid	Solid	39.3	22.4	Excel.	3.9	0.06	-0.48	0.75
6. Diallyl phthalate	Liquid	Solid	Solid	8.3	3.9	Fair	2.2	0.02	+0.36	0.044
7. Diallyl isophthalate	Liquid	Solid	Solid	10.6	7.6	V. Good	0.74	0.10		
8. Diallyl fumerate	Liquid	Liquid	Solid	12.7	5.9	Fair	2.6	0.02		
9. Diallyl maleate	Liquid	Liquid	Solid	13.4	9.8	Good	2.4	0.4		
10. Triallyl phosphite	Liquid	Liquid	Sooty Foam	37.0	34.4	Good	2.4	0.14		
11. N-Vinylpyrrolidinone	Liquid	Solid	Foam	10.6	7.3	Fair	3.0	0.02	-1.14	0.14
12. 4-Vinylpyridine	Liquid	Solid	Foam	11.6	7.4	Fair	0.6	0.13	-0.28	1.0
13. 2-Vinylquinoline	Liquid	Liquid	Solid	5.8+	--	--			-0.82	3.79
14. 2,5-Dimethylstyrene	Liquid	Liquid	Solid	4.0	2.8	Good	0.37	0.08	-0.96	0.97
15. Tetraethyleneglycol dimethacrylate	Liquid	Solid	Solid	2.0	1.8	Poor	0.18	0.06		
16. Ethylene dimethacrylate	Liquid	Solid	Foam	7.2	3.7	Fair	1.1	0.03		
17. p-t-Butylstyrene	Liquid	Solid	Foam	6.0	3.2	Fair	0.37	0.16	-0.9	1.37
18. 2-Vinylpyridine	Liquid	Liquid	Solid	1.3	--	--	--	--	-0.50	1.30
19. Glycidyl methacrylate	Liquid	Liquid	Solid	5.0	2.5	Poor	1.1	0.02		
20. 1,2,4-Trivinylcyclohexane	Liquid	Liquid	Liquid	9.5	0.8	Poor	0.18	0.04		
21. 5-Vinylnorbornene	Liquid	Liquid	Liquid	--	--	--	--	--	-0.46	0.045
22. Vinyltoluene	Liquid	Liquid	Solid	6.4	3.2	Poor	0.37	0.09		
23. 1-Allylimidazole	Liquid	Liquid	Liquid	1.4	0.3	--	--	--		
24. N-Vinylcarbazole	Solid	Solid	Foam	72.3	7.0	Good	1.5	0.05	-1.40	0.41
25. 9-Vinylanthracene	Solid	Liquid	Part Liquid	45.3	27.6	Poor	10.0	0.03	-1.60	0.90
26. 2-Methyl-5-Vinylpyridine	Liquid	Solid	Foam	25.0	10.0	Fair	3.1	0.03	-0.58	0.99
27. Bisphenol dimethacrylate	Solid	Solid	Solid	55.3	10.5	Fair	3.1	0.03		

Four of the monomers were evaluated separately from the others. The results of these later tests (Nos. 24 to 27) are also given in Table 2. Divinylbenzene was retested along with these four monomers as a control (data in parenthesis after No. 3). The later data for divinylbenzene at 400°-425°C look very good when compared to the previous data, however, the increase in char yield of divinylbenzene indicates that the test condition may not have been as severe as in the first tests. The data at 700°C are generally not as good as the better monomers examined previously. The exception to this is 9-vinylanthracene which produced a mushroom of nice looking fine cell low density carboneous foam at 700°C. This foam however had no mechanical strength.

These data were used to select promising monomers for additional weight loss studies using TGA analysis.

Table 2 also shows the Alfrey and Price Q/e values* for a number of these unsaturated monomers. These data are plotted in Figure 2. The "Q" value is a measure of the stability of the free radical, while the "e" value is a measure of the electrical nature of the molecule. Q/e values are used to indicate as to whether two monomers will readily copolymerize under free radical conditions. For an ideal alternating copolymerization, the two monomers must have similar Q values and the "e" values must have opposite signs.

Typical fumaric acid polyester resins have a positive "e" value and "Q" values of one or slightly greater. Thus, styrene with Q/e values of 1.0 and -0.8 is an excellent coreactant for fumaric acid polyesters while a monomer like methyl methacrylate (MMA) with Q/e values of 0.74 and +0.4 shows little tendency to copolymerize with fumaric acid polyesters if it is the only coreactant. However, if styrene is added to the fumaric acid polyester/MMA blend, good polymers are produced because it has an opposite sign on the "e" value, and can therefore readily coreact with both of the other monomers.

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*Additional information on the Q/e system can be found in many polymer or polyester texts (Reference 10).

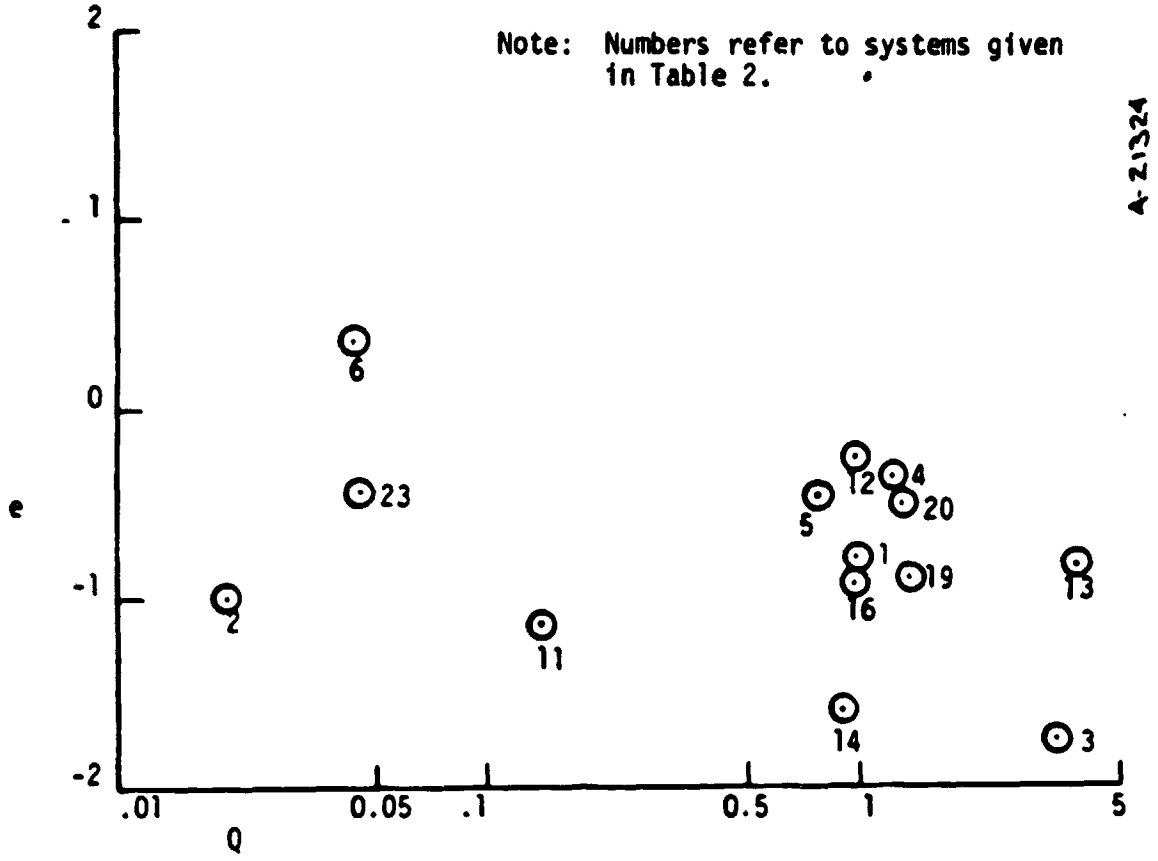

Figure 2. Plot of Q & e values for various monomers

Figure 2 shows that most of the vinyl monomers plotted have a reasonable Q/e value for copolymerization with fumaric type polyesters. The poorest choice of vinyl monomers appears to be N-vinyl pyrrolidinone which has a rather low Q value. Allyl monomers have still lower Q values and copolymerize well only with other allylic type polymers.

The polymers from the isothermal weight loss study given in Table 2 which showed the smallest weight losses were tested further using the TGA technique in static air. Figures 3 through 14 show the weight loss curves generated at a heating rate of 10°C/minute on 40 mesh samples (cured with the previously described mixed catalyst system). For comparison, high molecular weight (commercial) polystyrene was also run in static air and two of the better monomers (triallyl cyanurate and divinylbenzene) were run under

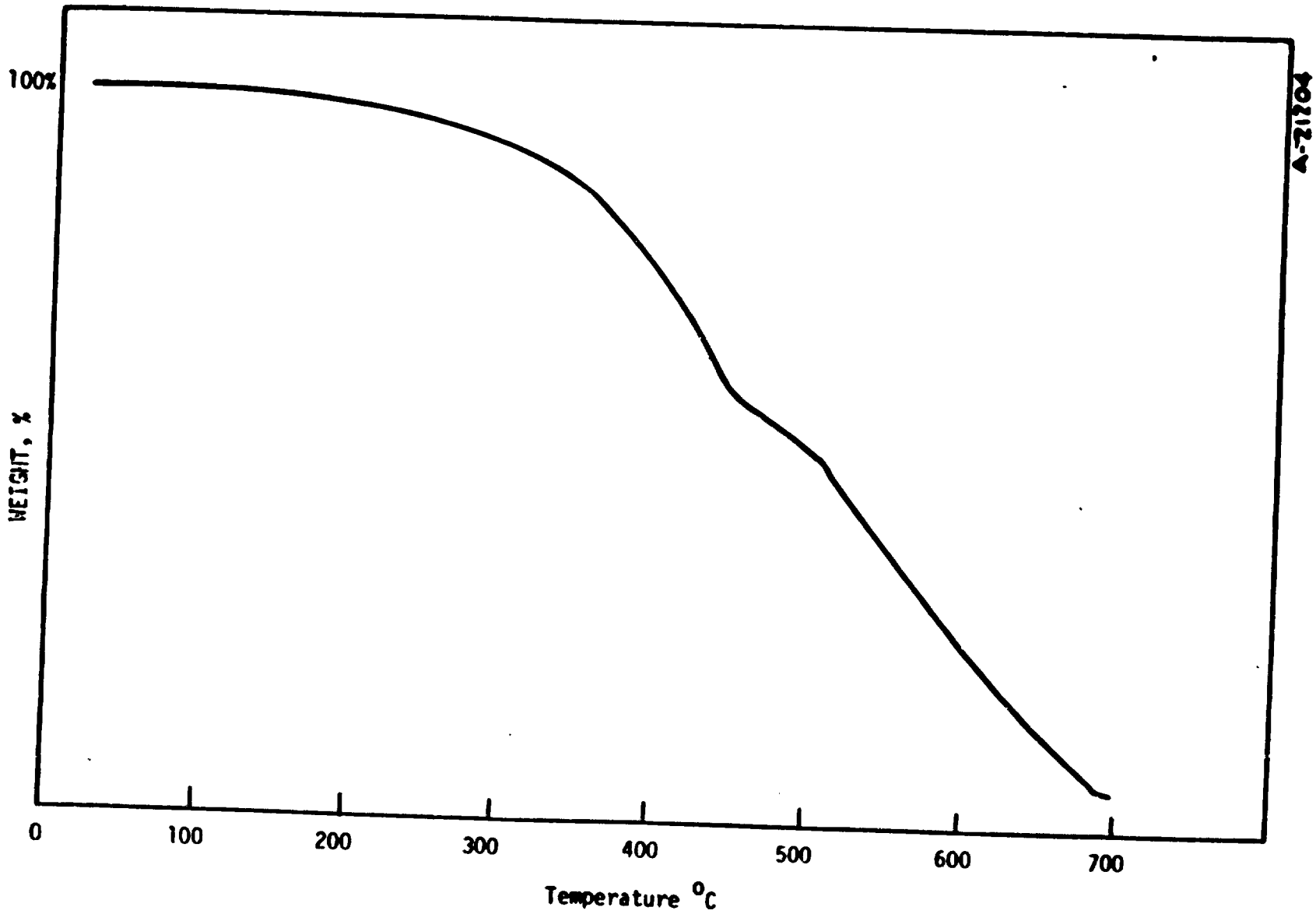

Figure 3. TGA analysis of polydivinylbenzene in air.

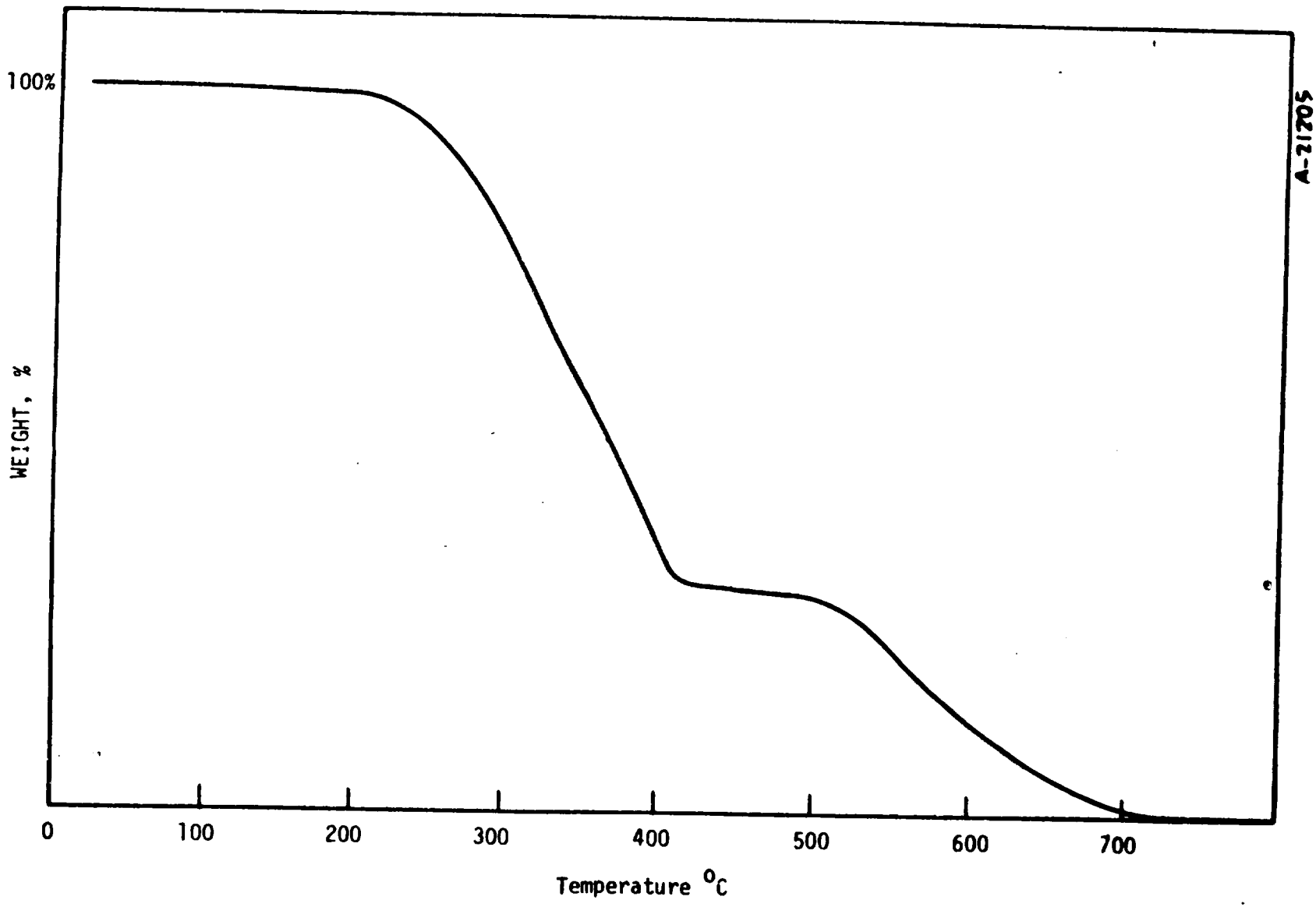

Figure 4. TGA analysis of poly 2-vinylnaphthalene in air.

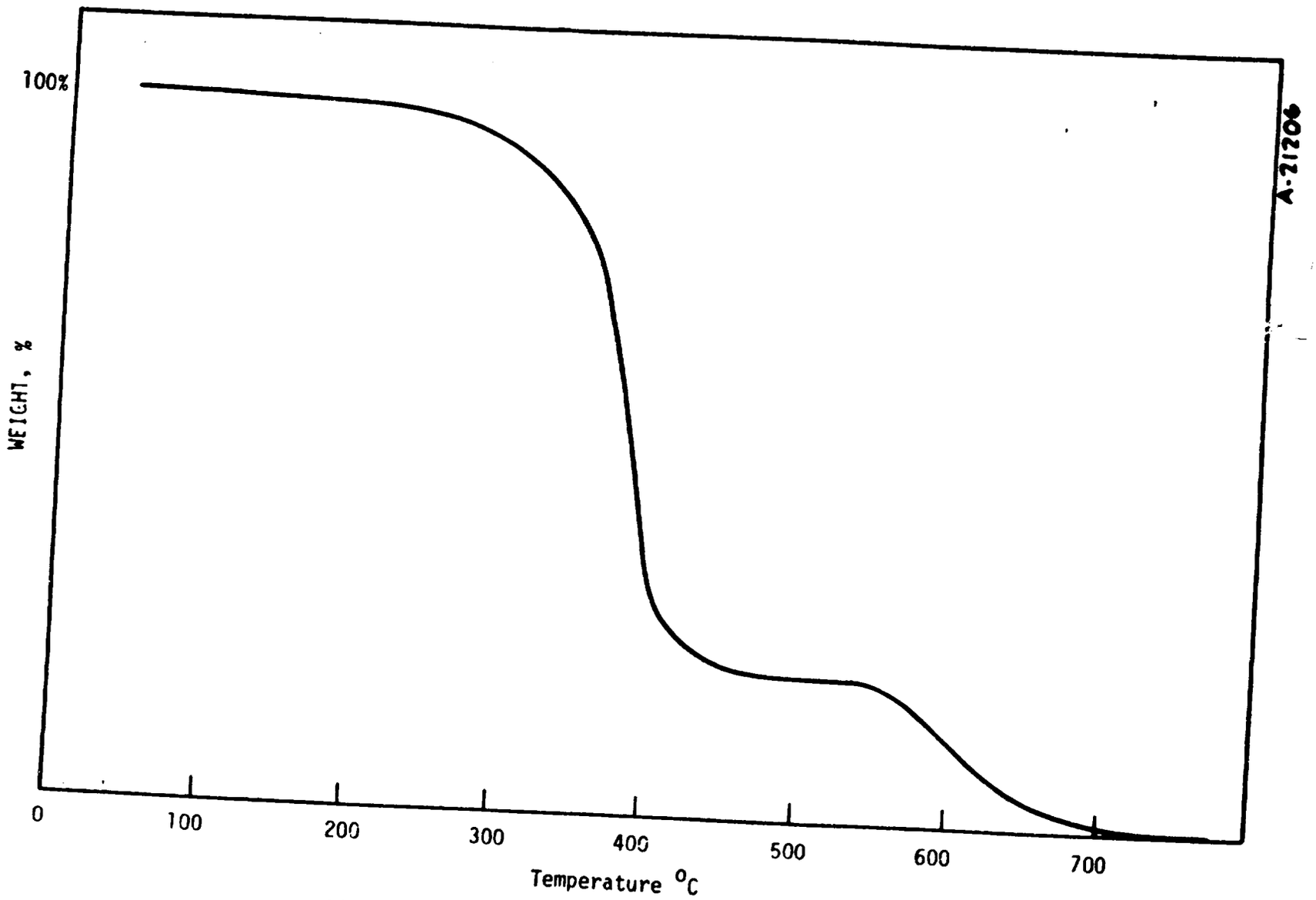

Figure 5. TGA analysis of poly 4-vinylbiphenyl in air.

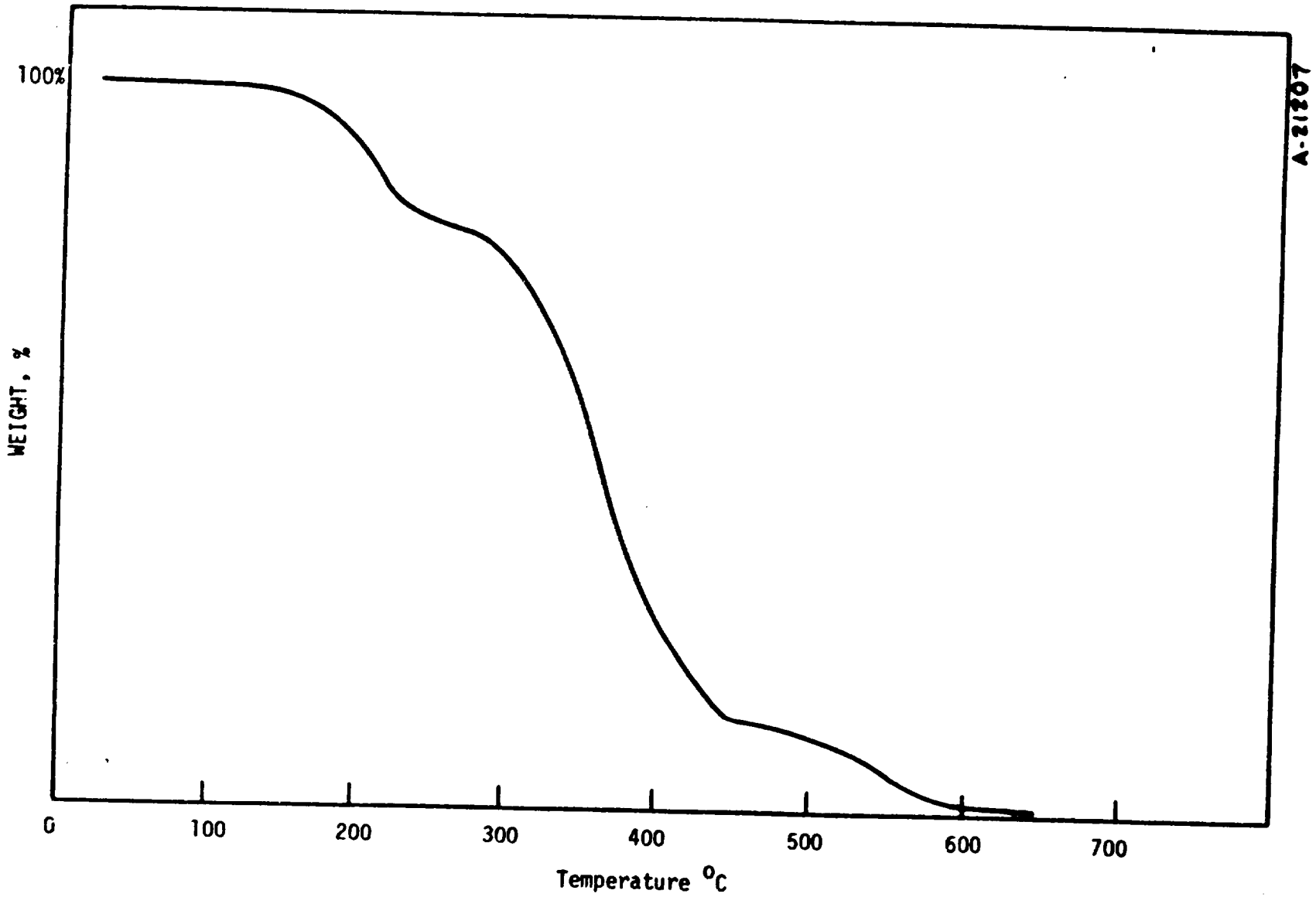

Figure 6. TGA analysis of polydiallyl phthalate in air.

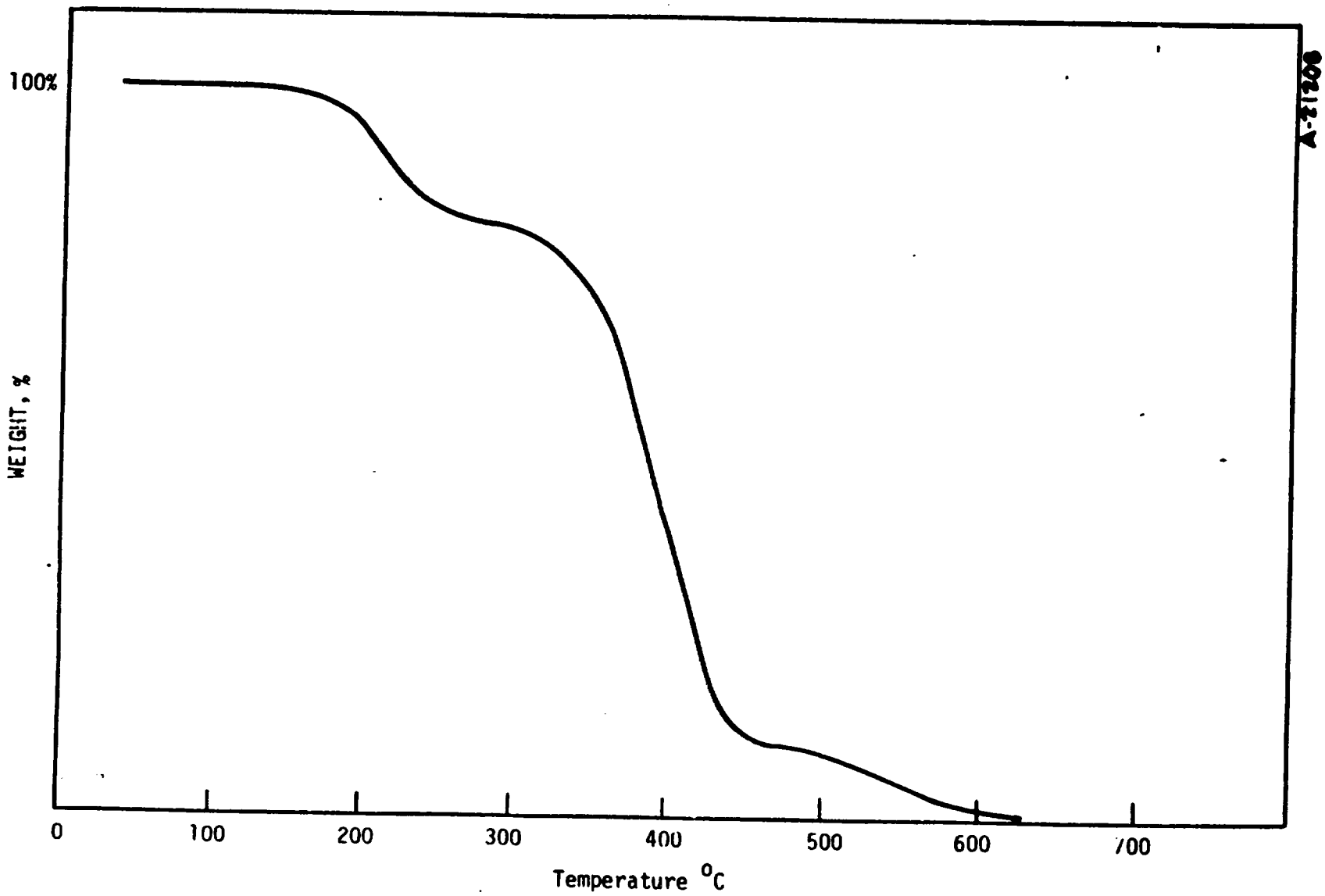

Figure 7. TGA analysis of polydiallyl isophthalate in air.

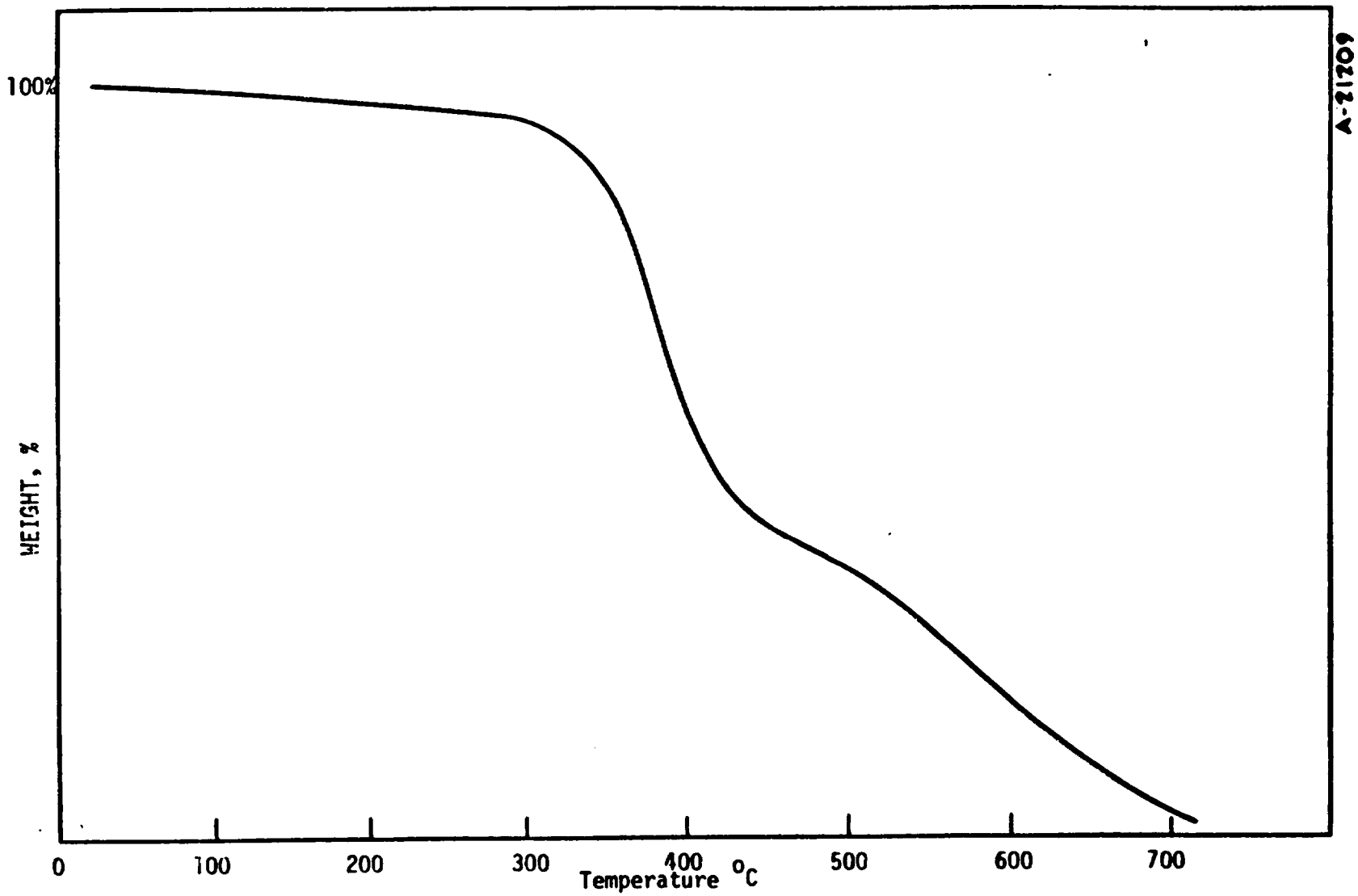

Figure 8. TGA analysis of polydiallyl maleate in air.

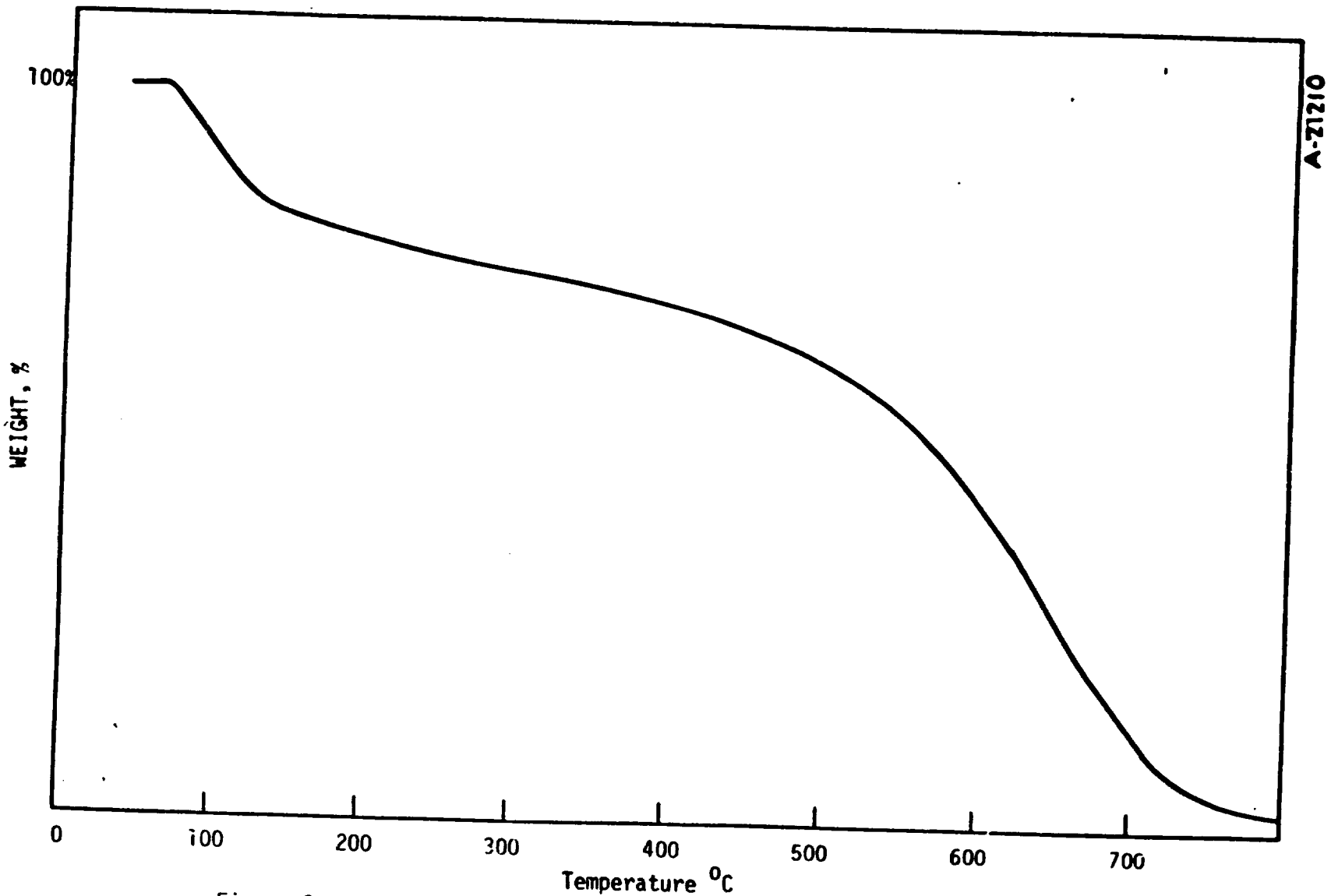

Figure 9. TGA analysis of polytriallyl phosphite (black soot) in air.

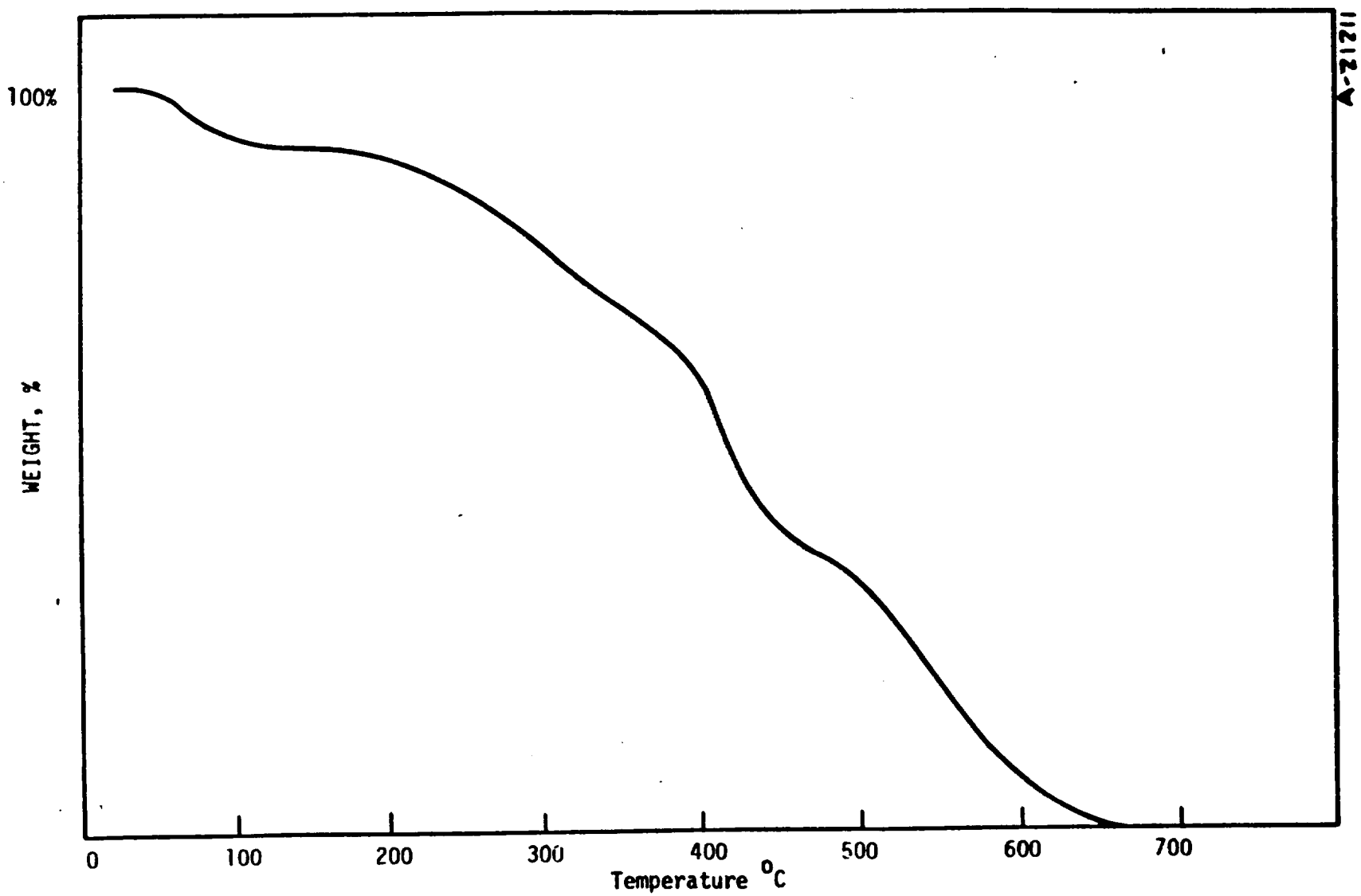

Figure 10. TGA analysis of poly n-vinylpyrrolidinone in air.

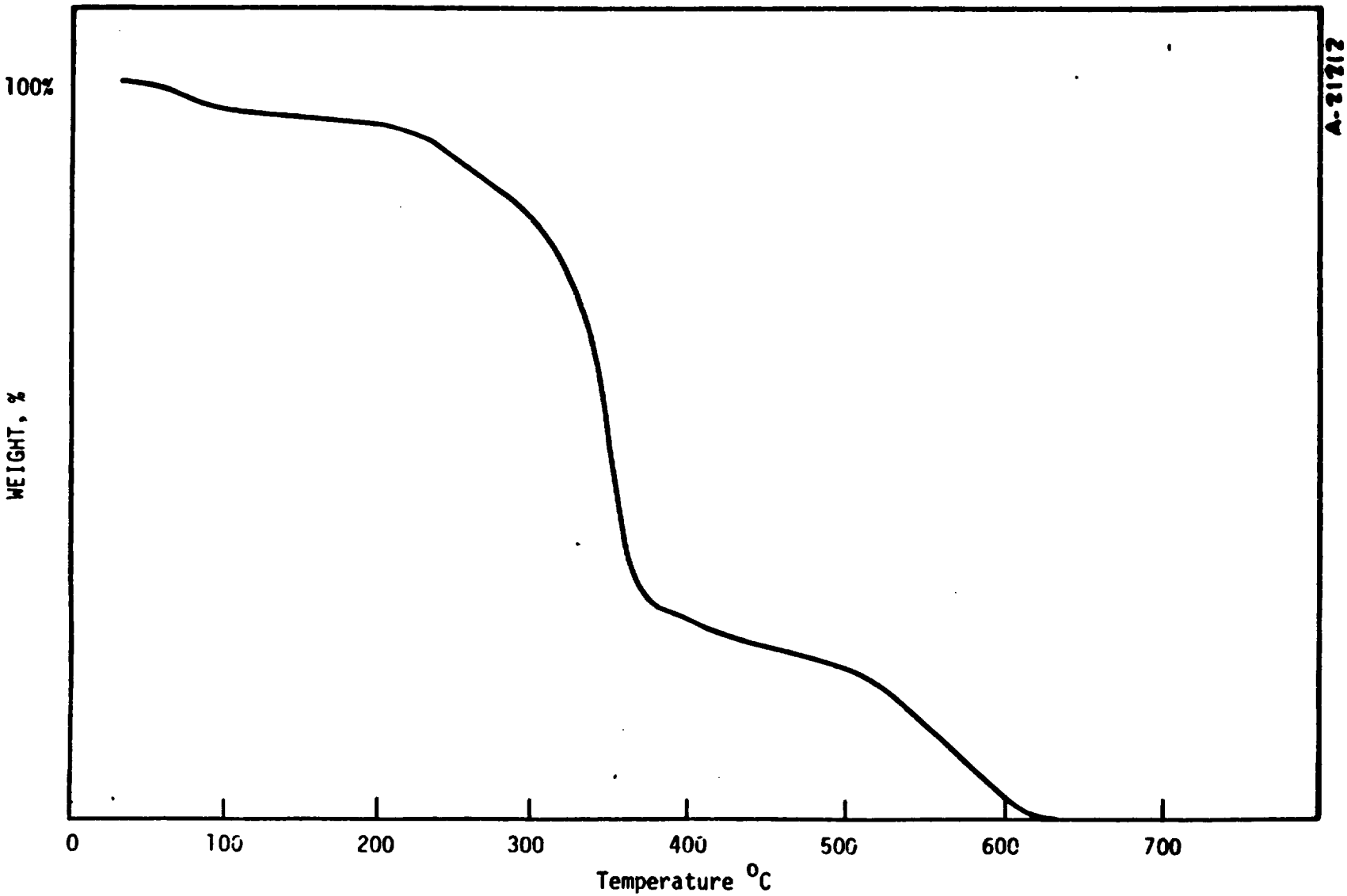

Figure 11. Poly 4-vinylpyridine in air.

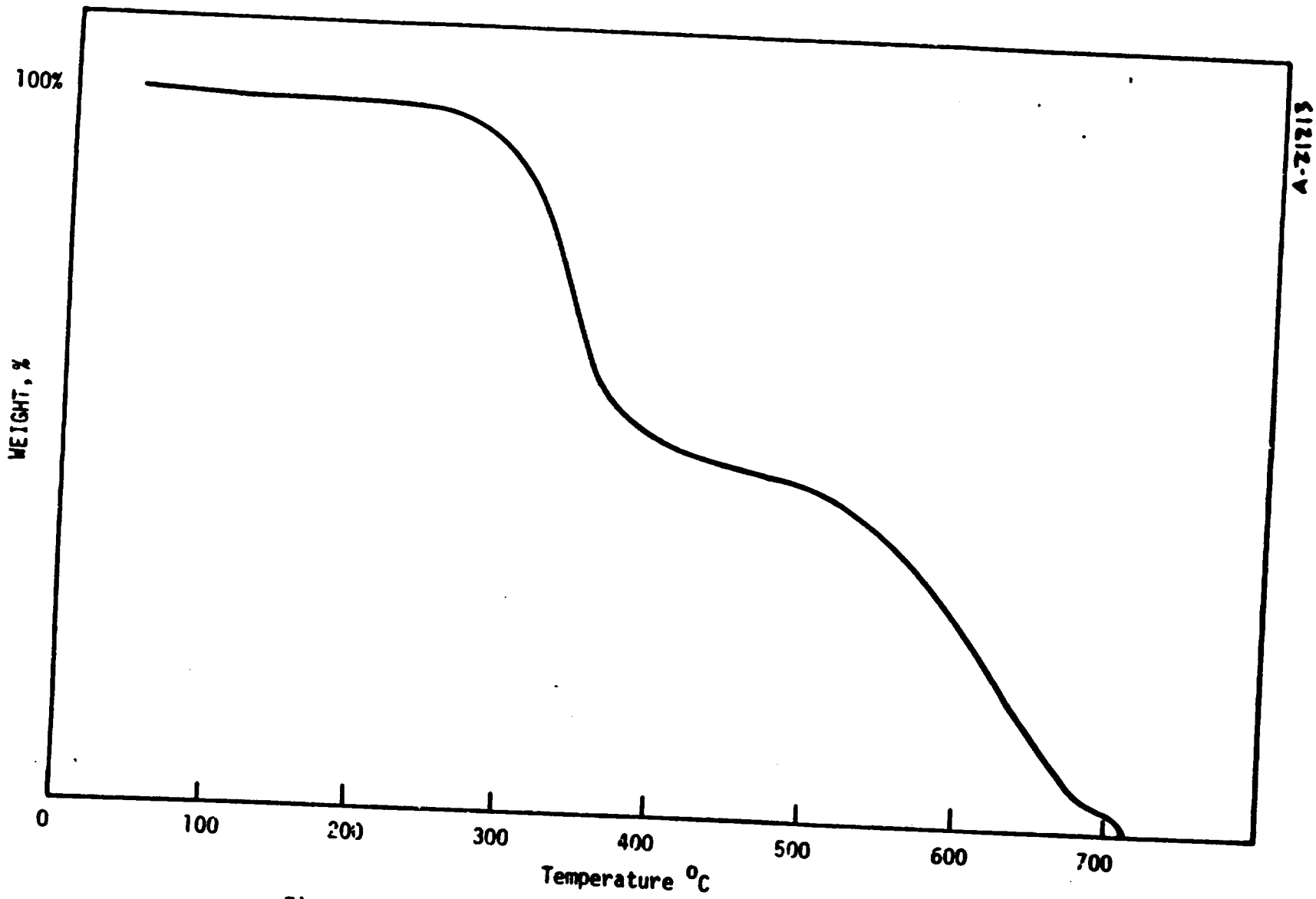

Figure 12. TGA analysis of poly 2-vinylquinoline in air.

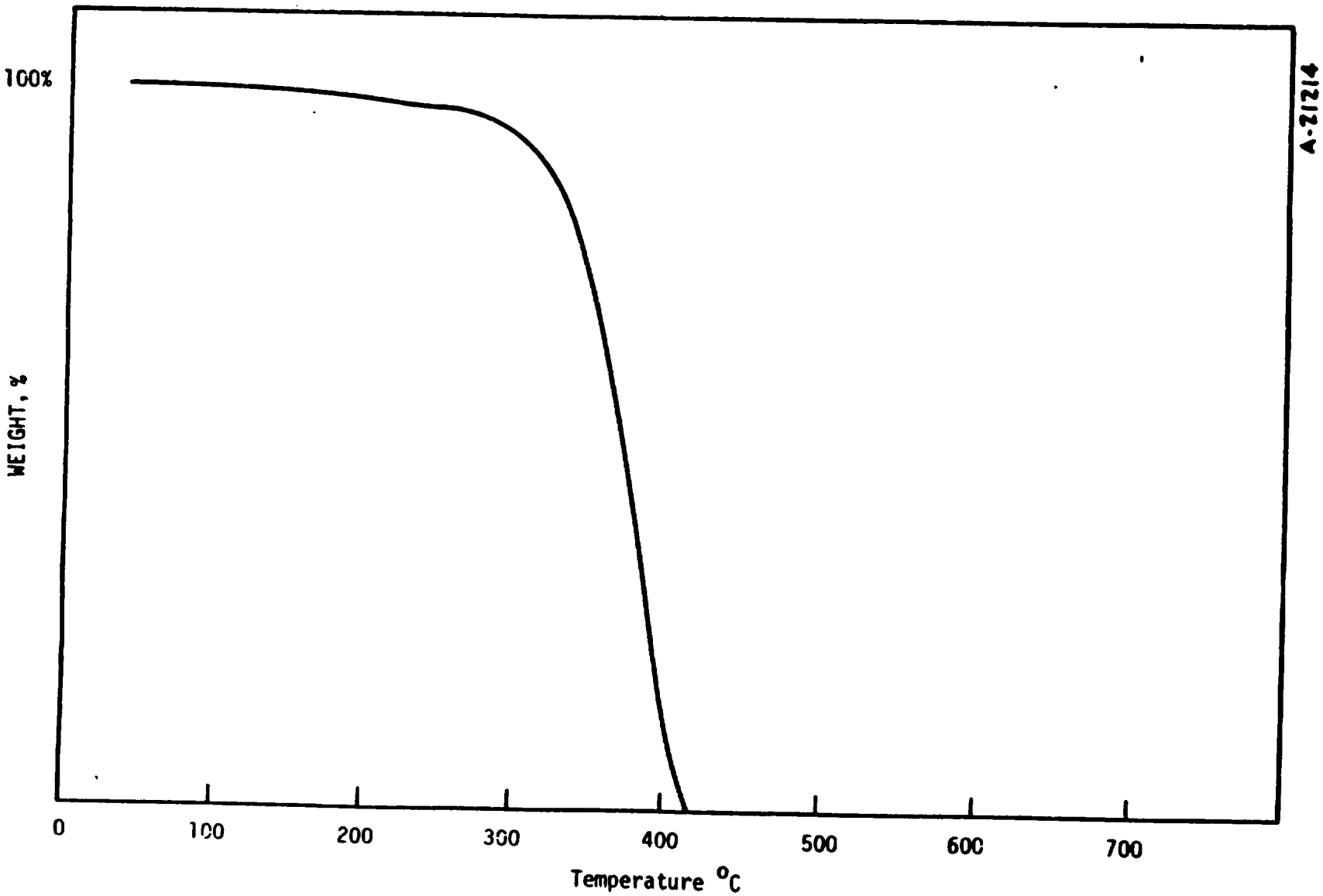

Figure 13. TGA analysis of polystyrene (high-molecular weight) in air.

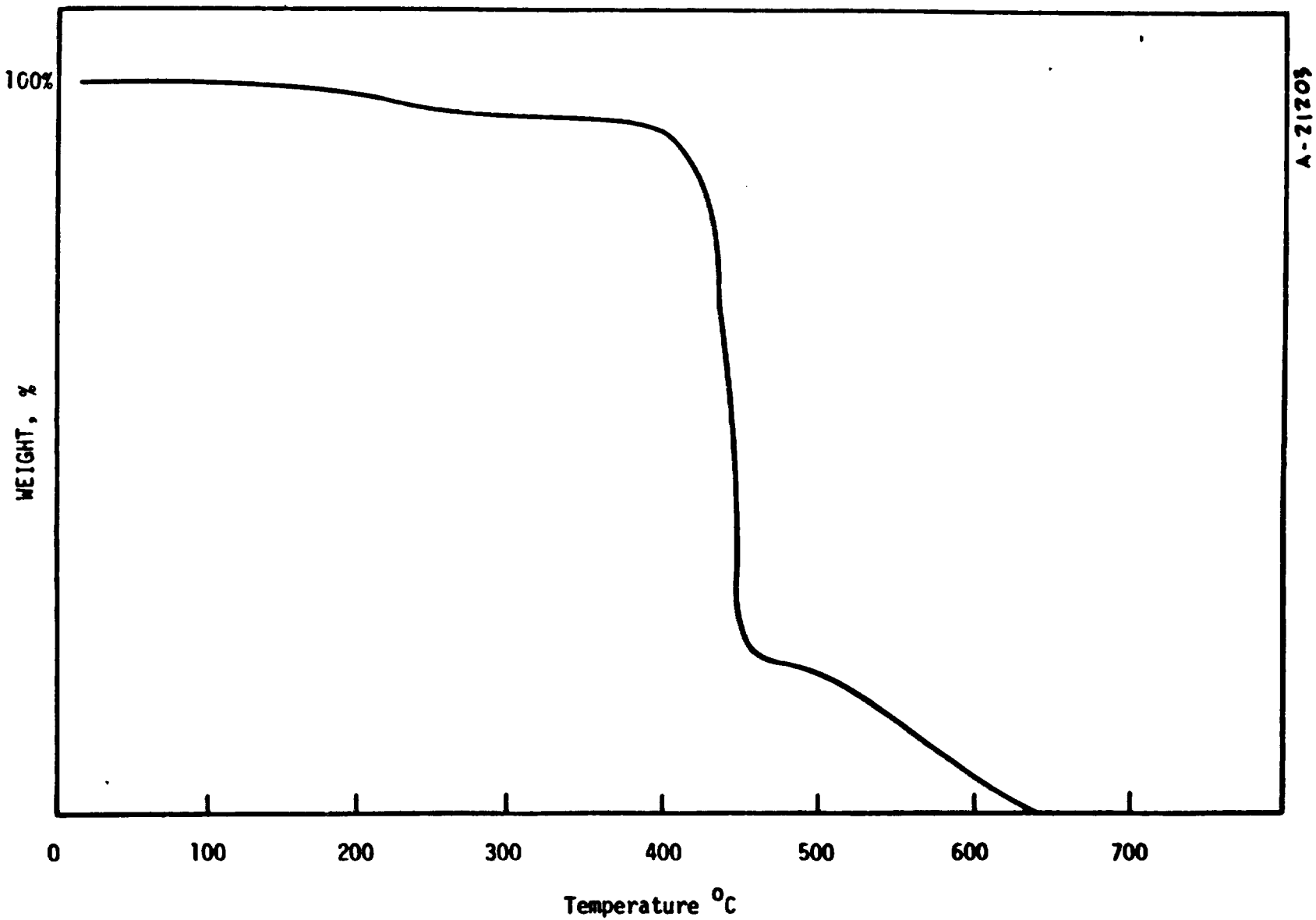

Figure 14. TGA analysis of polytriallyl cyanurate in air.

nitrogen (Figures 15 and 16).

Polytriallyl cyanurate (Figures 14 and 16) cured to a hard brittle polymer and had a significantly improved TGA curve compared to high molecular weight polystyrene. This monomer should produce good properties when blended with allyl endcapped polyester resins, however, it can only be used in small quantities as a comonomer in fumaric acid polyester resins.

Polydivinylbenzene TGA curves are shown in Figures 3 and 15. This material also gives significantly better weight retention than polystyrene in these tests and should make an excellent replacement for styrene in fumaric polyesters. The possible disadvantages with this monomer are that it has very high cure shrinkage and is much more reactive than styrene and therefore tends to make unstable blends with polyester resins. The sample used in this test was commercial grade which was 55 to 60 percent divinylbenzene (unspecified isomer ratio) with the remainder being mostly ethylvinylbenzene and some diethylbenzene.

Triallyl phosphite cured to a soot-like foam when gradually heated to 175^{o}C under nitrogen. If this material is used as a comonomer in polyester formulation in very small quantities, it is expected to act as a catalyst for char formation.

The diallyl phathalate (DAP) and isophthalate polymers did not achieve full cure after two hours at 175^{o}C using three percent dicumyl peroxide initiator. The samples were somewhat flexible and did not have the usual hardness of DAP resins. This is also reflected in their relative poor TGA curves (Figures 6 and 7).

The 4-vinylbiphenyl and the 2-vinylnaphthalene monomers are both solids at room temperature, but melted well before they cured making them excellent candidates for use in a system that is solid at room temperature. They could also be used as a comonomer with other liquids.

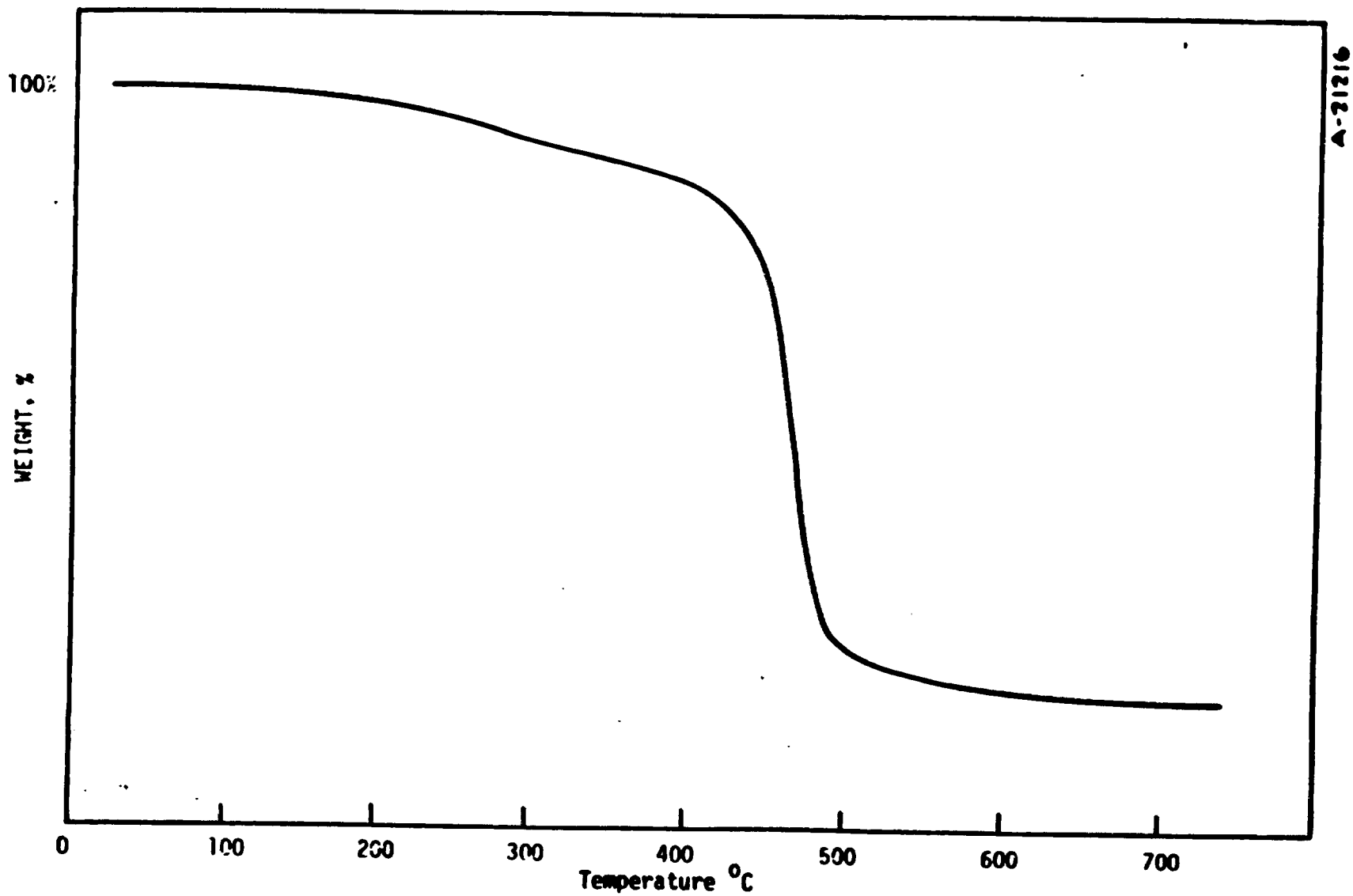

Figure 15. TGA analysis of polydivinylbenzene under nitrogen.

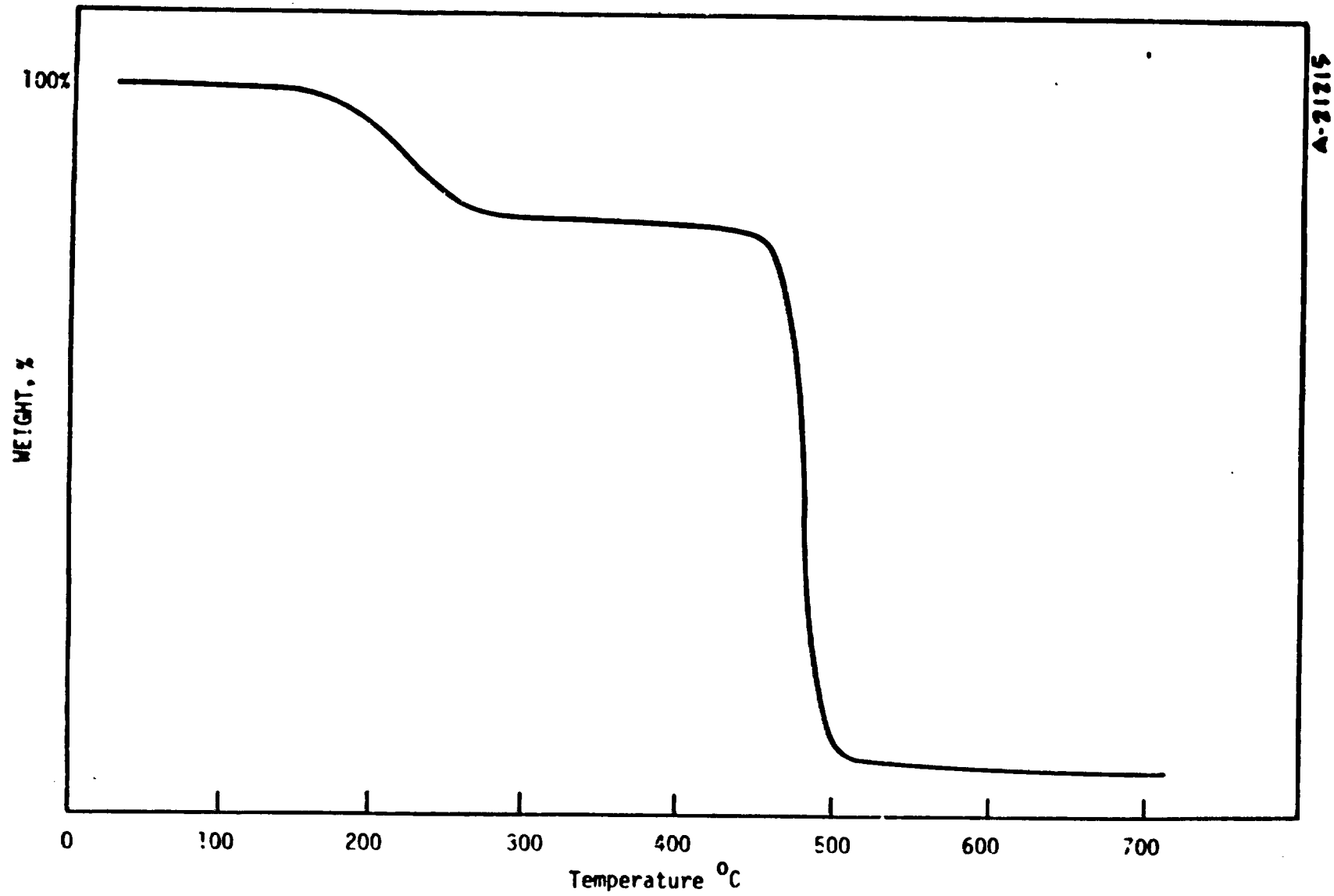

Figure 16. TGA analysis of polytriallyl cyanurate under nitrogen.

It can be seen from examining the data that optimum cures of the monomers were not achieved in many cases. For example, diallyl fumarate evaporated, rather than cured, in the open container with mixed peroxide initiators. Also examination of a number of the TGA curves show an initial weight loss that is due to loss of unreacted monomer. This free monomer is typical of free radical cures, however, the quantity of free monomer can usually be reduced to acceptable levels by selection of the proper initiator system and cure cycle. If proper cures can be achieved with the monomers, and with additional crosslinking from incorporation of multifunctional polyester backbones, improved performance from these materials would be expected.

PREPOLYMER - MONOMER BLENDS (RESINS)

Solubility Studies

The solubility of 18 polyester prepolymers in reactive monomers selected on the results presented in the previous section is shown in Table 3. These data show solubilities at various prepolymer concentrations as well as at both elevated and room temperatures. The elevated temperature solubility determinations were from testing one gram of material in a glass vial placed on a 150°C hotplate for one to five minutes. Sample testing was complicated by some of the samples gelling (without peroxide) and the monomer evaporation.

The data show that the polyester prepolymers made with naphthalene dicarboxylic acid (P2, P3, P4 and P5) are particularly insoluble when compared with the other prepolymers, and the higher the ratio of the naphthalene dicarboxylic acid to fumaric acid; the less soluble the polymer. The incorporation of $\emptyset POCl_2$ into the prepolymer reduces its solubility in the solvents tried.

The relative solubilities of various ratios of equivalent 2,7-naphthalene diol and BHPF polymers (P13, P15, P16, P17, and P18) indicate that the prepolymer is most soluble at a naphthalene diol/BHPF mole ratio of 1.5/3.5 (P16).

TABLE 3. SOLUBILITIES OF POLYESTER PREPOLYMERS IN UNSATURATED MONOMERS AT ELEVATED AND ROOM TEMPERATURE

PREPOLYMER CODE (SEE TABLE 1)	REACTIVE MONOMER																																			
	DIVINYLBENZENE			TRIALLYL CYANURATE			DIALLYL ISOPHTHALATE			DIALLYL PHTHALATE			DIALLYL FUMERATE			DIALLYL MALEATE			2-METHYL-4-VINYLPYRIDINE			N-VINYLQUINOLINE			N-VINYLCARBAZOLE			4-VINYLBIPHENYL			STYRENE		
	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*	HOT	RT	PERCENT*
P1	S	I	10	VS	S	10	VS	PS	10	VS	PS	10	S	I	10	VS	PS	10	S	PS	10														
P1	I		70	VS		60	VS		60																										
P2	PS	A	10	PS	PS	10	PS	I	10	I	I	10	I	I	10	I	I	10	PS	PS	10														
P2	I		70	I		60	PS		60																										
P3	PS	A	10	PS	PS	10	PS	I	10				PS	I	10	PS	PS	10	PS	PS	10	PS	B	10	I	A	10								
P3	I		70	PS		60	PS		60																										
P4	I		70	I		60	PS		60																										
P5	I		70	I		60	I		60																										
P6	S	I	10	PS	PS	10	S	PS	10				PS	I	10				S	PS	10	S?	B	10	I	A	10								
P6	PS	I	60	PS	PS	60	PS	PSB	60										PS	PS	33							S	SB	33	S	PS	70		
P7	S	A	10	VS	S	10	VS	S	10				S	PS	10				VS	VS	10	PS?	B	10				S	B	10					
P7	PS		70	PS		60	PS		60																										
P8	PS		70	PS		60	PS		60																										
P9	PS	A	10	S	S	10	S	PS	10				PS	I	10				S	PS	10	S	C	10				S	B	10					
P9	PS		70	S		60	S		60																										
P10	PS		70	S		60	S		60																										
P12	S	PS	60	S	SB	60	S	PS	60										S	PS	33							S	IB	33	VS	S	70		
P13	PS	I	60	S	SB	60	S	PS	60										S	PS	33							S	IB	33	VS	S	70		
P14	PS	I	60	S	SB	60	S	I	60										S	PS	33							S	IB	33	S	S	70		
P15	VS	S	60	S	SB	60	VS	SB	60										S	S	33							S	IB	33	VS	VS	70		
P16	VS	S	60	VS	SB	60	VS	SB	60										VS	VS	33							S	IB	33	VS	VS	70		
P17	S	S	60	S	SB	60	S	S	60										S	S	33							S	IB	33	VS	S	70		
P18	S	S	60	S	SB	60	S	SB	60										S	S	33							S	IB	33	VS	S	70		

* Weight percent prepolymer in mixture.
A Mixture exothermed and gelled during heating.
B Mixture is solid at RT.
C Mixture is semisolid at RT.
I Insoluble.
PS Partially soluble.
S Soluble.
VS Very soluble.

A similar comparison of phthalic acid/diphenic acid mole ratios in prepolymers P12, P13, P14, and P6 shows that higher concentrations of diphenic acid generally improve the solubility of the prepolymer in the monomer.

Prepolymers with high 2,7-naphthalene diol contents tend to only be soluble hot whereas, prepolymers with high BHPF contents remain soluble at room temperature. Their blends in diallyl phthalate and triallyl cyanurate freeze rapidly at room temperature to make clear glassy resins while similar blends in styrene and divinyl benzene solidify overnight.

Further solubility studies with prepolymer P16 show that it is readily soluble hot at 75 weight percent in a styrene/TAC/DVB blend but that solubility becomes marginal when the concentration is increased to 85 percent.

Char Properties

Char yields obtained on early prepolymer/reactive monomer blends (cured) are given in Table 4. The test was run in one dram vials by the same method described with the monomers in the previous section. This method produces a static air environment which is intermediate in severity between air and inert environments. The test has the advantage however that it somewhat represents the case wherein a burning laminate is exposed to air on the surface, but not in the interior of the laminate.

The data between the divinylbenzene and two allyl monomers are not strictly comparable as the two groups were run at different times, with different sample sizes and with different monomer ratios.

The best char yields were obtained with naphthalene dicarboxylic acid resins (P2 - P5). However, as reported above these materials are insoluble in the monomers employed and the resulting "cured" polymers did not fuse together, making them unprocessable unless a better solvent system could be found.

TABLE 4. CHAR YIELDS OF CURED POLYESTER PREPOLYMER/MONOMER BLENDS

Prepolymer	Divinylbenzene (30%) 1 Gram Samples				Triallyl Cyanurate (40%) 0.5 Gram Samples				Diallyl Isophthalate (40%) 0.5 Gram Samples			
	1 hr @ 400°C + 10 min @ 700°C		+ 1 hr @ 700°C		1 hr @ 400°C + 10 min @ 700°C		+ 1 hr @ 700°C		1 hr @ 400°C + 10 min @ 700°C		+ 1 hr @ 700°C	
	Yc (%)	Appearance (1)	Yc (%)	Appearance (1)	Yc (%)	Appearance (1)	Yc (%)	Appearance (1)	Yc (%)	Appearance (1)	Yc (%)	Appearance (1)
P1	31	F st	17	F Md	19	F wk	7	F wk	20	F wk	6	F wk
P2	51	Sd Vst	42	Sd Vst	32	F wk	16	F wk	13	F wk	1	F wk
P3	50	F st	41	F Vst	32	F wk	18	F wk	31	F wk	14	F wk
P4	54	F st	27	F Md	35	F wk	18	F wk	34	F wk	16	F wk
P5	62	Sd Vst	50	Sd Vst	40	F wk	25	F wk	35	F wk	19	F wk
P6	36	F st	9	F Md	23	F Md	13	F wk	21	F wk	7	F wk
P7	40	Sd Vst	33	Sd Vst	24	F Md	11	F wk	30	F Md	18	F wk
P8	49	F st	30	F Md	32	F wk	20	F wk	28	F wk	11	F wk
P9	42	F st	29	F Md	28	F wk	16	F wk	22	F wk	8	F wk
P10	40	F st	24	F Md	24	F wk	11	F wk	21	F wk	9	F wk

(1) F = foam, Sd = solid (not foamed), Vst = very strong, st = strong, Md = medium, wk = weak strength.

Good char yields were also obtained by incorporation of phosphorus into the polymer (P8 - P10). The data show increasing char yields with increasing phosphorous content.

The polymer (P7) based on 9,9-bis(4-hydroxyphenyl)fluorene gave generally better char yields than the equivalent naphthalene diol polymer (P4) and resulted in a stronger char. This stronger char is considered an important property necessary to keep the burning composite together. Based on these data, it therefore appears that the fluorene derivative is preferable over naphthalene diol for the purposes of this program.

Triallyl cyanurate also generally gives improved char yields when compared with diallyl isophthalate (DAIP). Since the cyanurate also is somewhat better solvent for most of the resins tested, DAIP was eliminated as a primary unsaturated monomer candidate.

TGA analyses in air and nitrogen were run on additional cured prepolymer-monomer blends. Test results are summarized in Table 5. Typical TGA curves are shown in Figures 17 and 18. The data show char yields up to 25 percent at 800°C under nitrogen without any significant difference resulting from a wide variation of mole ratios of polyester reactants, including increasing phthalate/diphenate ratios (Prepolymers P12, P13, P14, and P4) and increasing 2,7-naphthalene diol/BHPF ratios (Prepolymers P15, P16, P17, and P13).

The data also show that DVB and TAC monomers when tested neat do not provide char yields at 800°C. Blends of prepolymers with other monomers give char yields approximately in proportion to the prepolymer content of the mixture.

This indicates that all or most of the blended resins char is from the polyester prepolymer portion of the system. Consequently, based on a monomer free system, the polyester portion of the resin is estimated to have a char yield of about 40 percent. The overall char yields of prepolymer-monomer blends can therefore be increased above 25 percent by reducing the

TABLE 5. TGA ANALYSIS OF CURED POLYESTER RESINS (15°C/MINUTE)

Composition		Aerobic Char Yield, %				Anaerobic Char Yield, %	
Prepolymer	Monomer (% Monomer) (1)	300°C	400°C	500°C	600°C	500°C	800°C
P12	DVB (40)	86	65	36	8	27	23
P13		75	52	34	4	27	22
P14		81	65	37	11	30	25
P4		90	67	38	9	29	24
P15		91	62	39	14	30	24
P16		89	63	39	15	29	23
P17		86	64	41	16	30	25
P13		75	52	34	4	27	22
P12		86	65	36	8	27	23
P12	VBP (67)	92	62	24	9	18	14
P12	MVP (67)	89	57	28	15	13	11
P16	DVB (40)	89	63	39	15	29	23
P16	TAC (40)	87	61	39	11	21	17
	TAC (100)					15	0
	DVB (100)					36	0
Shell Epocryl 12 (2)	Styrene (30)					7	5
Silmar S389A (3)	Styrene (30)					5	2

(1) DVB = Divinylbenzene; VBP = 4-vinylbiphenyl; MVP = 2-methyl-5-vinylpyridine
TAC = triallyl cyanurate
(2) Acrylic acid endcapped epoxy resin.
(3) Commercial proprietary "heat resistant" polyester resin.

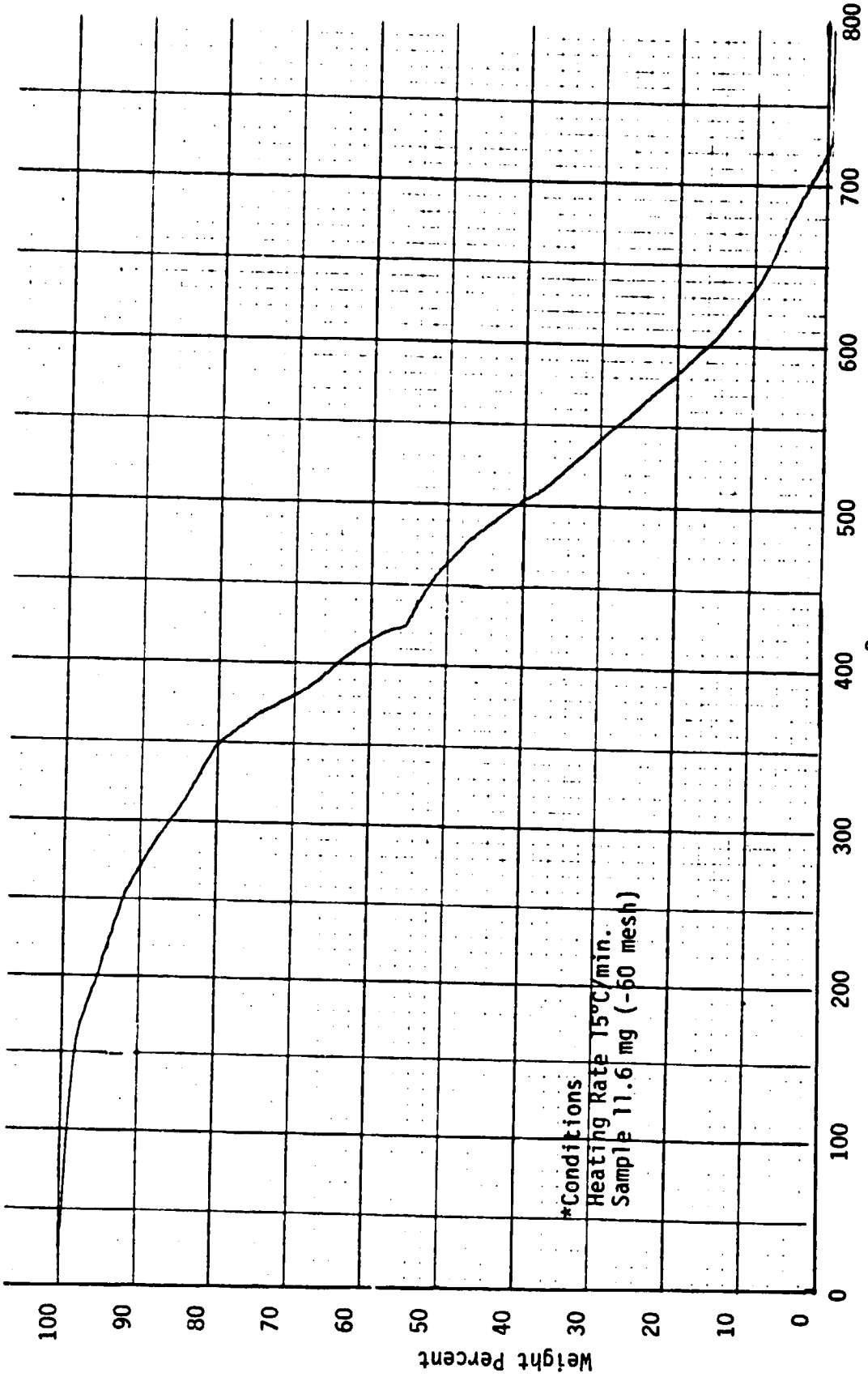

Figure 17. Typical TGA analysis of aromatic polyester in static air*.

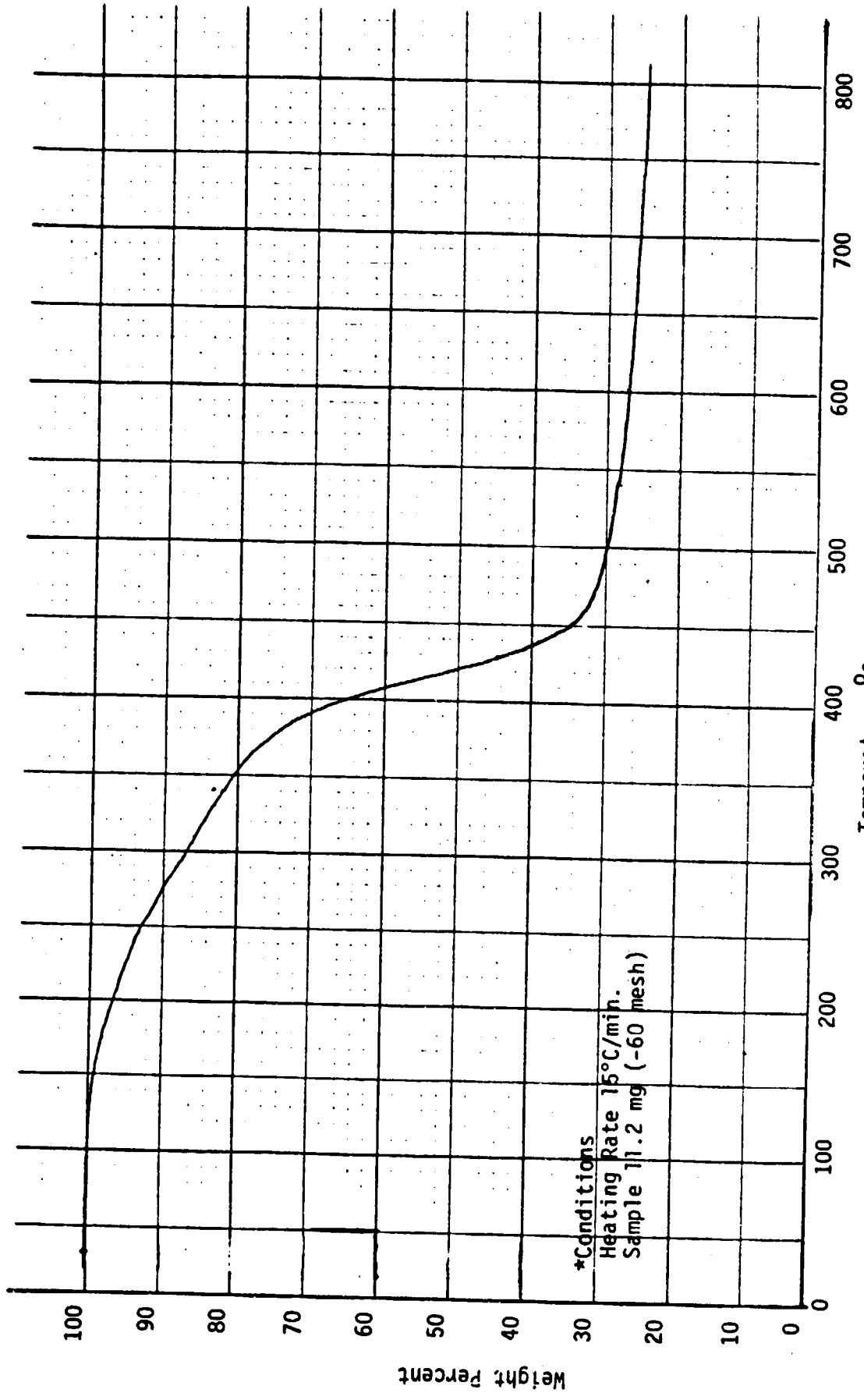

Figure 18. Typical TGA analysis of aromatic polyesters in nitrogen*.

monomer content of the blends. Char yields of 25 (or 40 percent) percent are about in the range expected for other addition cure resins such as epoxies, but represent a significant improvement over commercial polyester type materials such as Shell Epocryl 12 or Silmar S389A which are included in Table 5 for comparison.

Final Blend (Resin) Selection for Composite Evaluation

Prepolymer P16 was further evaluated at higher ratios with monomers to improve the char yield and to approach the same stoichiometry used in commercial polyester resins. The typical value of 30 weight percent monomer in commercial resins is equivalent to about 15 percent monomer in these aromatic polyester resins because of the higher molecular weights of the aromatic portions of the prepolymers.

It was found that styrene was the only monomer that would dissolve the prepolymer at these higher concentrations, and since it was previously observed that the monomer did not contribute to the char yield, the monomer of choice became styrene. It was also hoped that the styrene would reduce the brittle nature of resin system. Quantities of TAC and DVB monomers were also added to increase the crosslink density and thereby to improve the thermal properties of the system.

The cured resins were characterized by DTUL* analysis and TGA. The results of these tests are summarized in Table 6. The cured resins were all dark and brittle. The resin with 80 percent polyester prepolymer had the greatest ambient toughness. However, it can be seen in Table 6 that the DTUL of this sample was significantly lower than resins with other monomer levels. Small samples of the resin with 75 percent polyester prepolymer would not support 3.1 MPa (449 psi) compressive load required for DTUL at RT (brittle failure) and the DTUL was determined at 0.6 MPa (90 psi).

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*DTUL = Distortion Temperature Under Load (See Appendix A).

TABLE 6. COMPARISON OF POLYESTER RESIN PROPERTIES

Compositions[3]				DTUL	Aerobic Char @				Anaerobic Char @	
Prepolymer P16 (%)	TAC (%)	DVB (%)	Styrene (%)		300°C	400°C	500°C	600°C	500°C	800°C
85	3	2	10	158°C[1]	98	77	56	10	48	41
85	6	4	5	148°C[1]	96	71	33	3	32	27
80	6	4	10	113°C[1]	97	69	53	10	46	38
75	6	4	15	144°C[2]	96	74	29	5	55	38

1. @ = 3.1 MPa (449 psi)
2. @ = 0.9 MPa (90 psi)
3. Cured with one percent USP-245 and one percent Lucidol 500% - Cured 30 minutes @ 80°C + 30 minutes @ 90°C + overnight at 200°C.

TGA analysis in air and nitrogen of the cured resins gave significantly better results (Y_c^{800} = 41 percent) than reported above (Y_c^{800} = 25 percent). The higher yields may be due to the higher cure temperature used with these samples (200°C instead of 180°C). At this temperature, unreacted styrene monomer can be expected to be lost from the cured polymer. The higher char yields also result from use of higher prepolymer levels in the Table 6 resins.

Curing Agent Studies and Selection for Final Blend (Resin)

Polyester resins are typically cured with an organic peroxide (free radical) initiator. Styrene containing polyester resins are most frequently cured with methylethylketone peroxide, or benzoyl peroxide, while allyl type polyester resins require a higher temperature cure and use a peroxide such as dicumyl peroxide. Numerous other peroxides are sold commercially that offer various advantages but these peroxides usually sell at a higher price.

To obtain optimum cures, it is normal to use two (or more) peroxides to smooth out the cure. Typically, a low temperature "smooth" peroxide is used to cause the resin to solidify, and a higher temperature "powerful" peroxide is used to complete the cure after the liquid phase can no longer evaporate and cause voids.

A study of various curing agents for aromatic polyester prepolymer-divinylbenzene, triallyl cyanurate, and styrene blends indicated that a combination of "USP-245" and "500T" peroxides gives a satisfactory smooth cure which results in a hard (brittle) polymer. The "USP-245" causes the system to gel between 70° to 90°C thus preventing blowing from volatilization of the unreacted monomers. This catalyst alone does not give hard cures particularly with allyl monomers. The final cure is accomplished with the "500T" peroxide at about 180°C. One disadvantage with this catalyst system is that the "USP-245" peroxide can be expected to limit the shelf life of the catalyzed resin. However, it was found that a 10 gram mass of the laminating resin did not gel in a week at ambient temperatures. The

other disadvantage is that the system is "air inhibited". If a dab of resin is allowed to rest undisturbed on an aluminum surface at 90°C, the unexposed (to air) material will gel in five to ten minutes, however, the same material will thicken but never gel if it is probed constantly under the same conditions.

An initial screening study to select a suitable peroxide initiator was run on various combinations of TAC and DVB, and eventually on P16 prepolymer-TAC-DVB blends. The studies were run on gram quantities of resin in one dram vials, using various peroxides levels and stepped cure cycles between 60°C and 180°C with an overall heating ratio of 2°C/minute. The peroxides that were evaluated are given in Table 7.

The data showed that "USP-245" gave the best results at low temperatures and "500T" gave the best cures at higher temperatures. Hard-clear cures were also achieved with "130", "USP-333", and "Vulcup R". The other peroxides resulted in foaming, or cheesy systems.

Combinations of TAC and DVB cured with USP-245 and 500T under similar conditions as above showed that a weight ratio of 60/40 TAC/DVB cured with one percent USP-245 and two percent 500T gave near optimum results. All the systems that cured hard and clear, also cracked or shattered due to the high cure shrinkage. When several polyester prepolymers (P6, P7 and P12) were added to the TAC/DVB blends or with styrene, at a 50 weight percent level, and the systems cured as shown, the samples no longer cracked. However, the resulting polymers were very brittle.

When the bulk of the monomer was replaced with styrene, it was necessary to re-evaluate the catalyst system, particularly because of the brittle nature of the cured polymer.

The USP-245 and Lucidol 500T catalyst system is designed for higher temperature cures which are needed with allyl monomers. Styrene based polyesters are typically cured at lower temperatures using MEKP (methylethylketone peroxide) or BZP (benzoyl peroxide) catalysts.

TABLE 7. ORGANIC PEROXIDES

Trade Name	Manufacturer	Chemical Name
Vulcup R	Hercules Inc.	α,α-Bis(t-butylperoxy)isopropylbenzene
500 R	Pennwalt Corp.	Dicumyl peroxide
101	↓	2,5-Dimethyl-2,5-bis(t-butylperoxy)hexane
130	↓	2,5-Dimethyl-2,5-bis(t-butylperoxy)hexane
Lucidol 98	↓	Benzoyl peroxide
Lucidol DTBP	↓	Di-t-butyl peroxide
CHP	↓	Cumene hydroperoxide
Lupersol DDM	↓	Methylethylketone peroxide
Esperox 10	Witco Chemical Corp.	t-Butyl peroxybenzoate
USP-245	↓	2,5-Dimethyl-2,5-bis(octanoylperoxy)hexane
Esperox 28	↓	t-Butyl peroctoate
USP 400P	↓	1,1-Bis(t-butylperoxy)cyclohexane
USP 333P	↓	Ethyl-3,3-bis(t-butylperoxy)butyrate

Six formulations were prepared representing combinations of two polyester backbones cured with MEKP, BZP and USP-245 catalysts. The combinations are shown in Table 8. The catalyst concentrations were selected based on the manufacturers recommendations. None of these formulations showed a substantial improvement in toughness over previous compositions, and the DTUL results (180°C cure) indicated that the USP-245 catalyst gave the best cure.

Based on these results, the USP-245 - 500T catalyst system was retained for use with the styrene monomer system. The 500T concentration was reduced to one percent since the resin no longer contained a high percentage of triallyl cyanurate.

GRAPHITE COMPOSITES

Fiber Selection

Thornel 300 (3000 count) carbon fiber was selected as the reinforcement for use in the polyester resin composites. This selection was made due to its general useage by the airframe industry.

A survey of carbon fiber manufacturers, including Union Carbide, Celanese, and Hercules, in an attempt to find a fiber with a polyester compatible size, was unsuccessful.

The development of a suitable polyester compatible size was beyond the scope of this program, however two modifications to the carbon fibers were contemplated. One modification was to react the epoxy finish on the fibers with acrylic or methacrylic acid to make the "vinyl ester". The other modification was to use heat cleaned fibers, however it was decided that these fibers would be too difficult to process.

Six composites were made using Thornel 300 fiber and polyester resin made with the P16 prepolymer and styrene. The physical properties of these composites are given in Table 9. The resin composition and typical

TABLE 8. NEW POLYESTER FORMULATIONS FOR PEROXIDE SELECTION

Polyester Prepolymer	Polyester Prepolymer PBW	Reactive Monomer* PBW	Peroxide Initiator PBW	Peroxide Type	DTUL, °C @ 3.1 MPa (449 psi)	Percent Aerobic Char				Percent Anaerobic Char	
						300°C	400°C	500°C	600°C	500°C	800°C
P16	83	17	1.0	BZP(98%)	92	90	65	46	2	38	33
P16	83	17	2.0	MEKP(60%)	85	90	66	46	3	41	32
P16	83	17	1.5	USP-245	97	90	68	47	6	44	37
P17	83	17	1.0	BZP(98%)	51	86	63	46	4	36	32
P17	83	17	2 0	MEKP(60%)	76	83	57	39	2	34	29
P17	83	17	1.5	USP-245	83	82	58	36	4	33	28

*Monomer compositions: 95 PBW styrene; 2 PBW divinyl benzene; 3 PBW triallyl cyanurate.

TABLE 9. PHYSICAL PROPERTIES OF POLYESTER-THORNEL 300 LAMINATES

ID	Size (cm)	Thickness (cm)	Specific Gravity	Void Content (Vol %)	Fiber (Vol %)	Resin (Wt. %)	Notes
1	10.2 x 10.2	0.368	1.49	2.0	53.8	36.4	
2	10.2 x 10.2	0.244	1.49	6.2	70.3	22.0	Delaminated corner
3	10.2 x 10.2	0.253	1.48	3.1	64.3	25.8	
4	20.3 x 20.3	0.236	1.54	0.6	64.5	22.9	
5	20.3 x 20.3	0.230	1.46	3.9	59.1	32.5	Dry fibers
6	15.2 x 15.2	0.233	1.50	0.8	58.3	33.2	

fabrication procedure used on all the composites is given in the experimental section of this report.

Due to difficulties in completing the vacuum impregnation at 150°F with the polyester prepolymer with 25 parts of styrene (25 parts styrene: 100 parts polyester prepolymer), the ratio of styrene was increased to 30 parts for prepreg preparation for laminates 3 through 6.

The general quality of the laminates is far from optimum. In flexural testing, they failed in shear. The failures appear to be caused by poor fiber wetting and/or low mechanical strength of the resin. Poor wetting of the fibers is likely to be caused by the lack of a polyester compatible sizing on the fibers. The UC 309 sizing on the T-300 fibers is epoxy compatible. The sizing may also inhibit the cure of the polyester resin. The fiber finish problem remains unresolved.

Another possible explanation for the poor shear strength is that too much styrene may be lost during the fabrication step. Without adequate monomer present, fumaric acid unsaturation is difficult to react under the cure conditions, and tends to dimerize rather than polymerize.

DTUL tests on the composites at 3.1 MPa (449 psi) showed that the composites are benefited by postcure. A sample from the 6" x 6" composite showed a DTUL of only 54°C after 175°C cure. Air postcure for one hour at 175°C raised its DTUL to 114°C and an air postcure at 200°C for one hour raised the DTUL to 135°C. With this postcure schedule however, the DTULs of all the composites were not the same. The DTULs of the composites ranged from a low of 116°C to a high of 135°C. Varying styrene contents in the composites may be the cause of this variation.

Based on these DTUL data the isothermal aging temperature and upper composite test temperature of 82°C (180°F) was selected. This temperature was also selected since many aircraft materials are evaluated and qualified for use at this temperature.

C-scan tests on the six composites were run at Automation Industries in Richmond, California. The tests were run using an Automation Industries Immerscope Model 721, using a 5 MHz transmitter (0.5 inch) and pulser and a 2.25 MHz receiver (0.75 inch). The tests were conducted at two power levels representing high and low sensitivity to voids. The two power levels were separated by 10 to 12 decibels. C-scans of the laminates are given in Appendix B. Figure B2A, at low sensitivity, shows a visible to the eye delamination in the lower right corner, it also shows the 6.3 x 6.3 mm metal reference in the upper left corner. A similar reference is also present in the lower right corner, but it is obscured by the delamination. Figure B2B shows the same composite at a 12 decibel increase in sensitivity. The image now shows increased void areas and voids parallel to the fiber direction, which are assumed to be unwetted fibers.

The other five composites provided similar scans. At low sensitivity, the composites are relatively free of imperfections, while at high sensitivity they show large void areas and significant quantities of unwetted fibers.

An attempt to correlate C-scan tests results on Laminate No. 4 with the mechanical property data discussed below (flexural testing) failed to show correlation.

Laminates 3, 4 and 6 were cut into flexure and shortbeam shear specimens, and postcured for one hour at 200^{o}C. Weight losses between 1.1 and 3.7 percent were observed during postcure which is likely due to styrene loss.

The specimens were split into eight groups for isothermal aging at 82^{o}C (180^{o}F). Specimens were removed from the aging oven after one week, three weeks and twelve weeks (2016 hours) and tested at both room temperature and 82^{o}C. The data obtained from the tests are presented in Tables 10 and 11. The highest shortbeam shear value obtained was 23.9 MPa (3500 psi), the highest flexural strength and modulus 619 MPa (89,800 psi) and 142.7 GPa (20.7 x 10^{6} psi) respectively. The flexural specimens failed in shear.

These values are unacceptably low and as previously discussed, thought to principaliy be due to poor fiber wetting. Isothermal weight loss data on a specimen from Laminate No. 6 at 82^{o}C over the same period varied between -0.03 and +0.01 percent without any discernable trend.

TABLE 10. MECHANICAL PROPERTIES OF POLYESTER-THORNEL 300 COMPOSITES TESTED AT ROOM TEMPERATURE AFTER AGING AT 82°C

Aging Time at 82°C	Panel ID	Shortbeam Shear			Flexural				
		Average Strength (MPa)	Std. Dev.	Number of Specimens	Average Strength (MPa)	Std. Dev.	Average Modulus (GPa)	Std. Dev.	Number of Specimens
Initial	4	17.6	1.72	3	581	75.2	110.3	3.8	4
	6	17.5	0.98	3	370	--	142.7	--	1
1 Week	4	16.9	1.64	3	530	92.4	105.5	13.1	4
	6	16.5	0.62	3	265	--	122.7	--	1
3 Weeks	4	19.9	2.96	3	550	57.3	118.6	5.2	3
	6	20.8	2.35	3	388	--	97.2	--	1
12 Weeks	4	16.3	0.14	3	619	43.9	120.4	3.1	3
	6	17.2	1.04	3	451	--	105.5	--	1

Note: To convert Pascals to psi, multiply by 1.45×10^{-4}.

TABLE 11. MECHANICAL PROPERTIES OF POLYESTER-THORNEL 300 COMPOSITES TESTED AT 82°C AFTER AGING AT 82°C

Aging Time at 82°C	Panel ID	Shortbeam Shear			Flexural				
		Average Strength (MPa)	Std. Dev.	Number of Specimens	Average Strength (MPa)	Std. Dev.	Average Modulus (GPa)	Std. Dev.	Number of Specimens
Initial	4	17.9	--	1	353	45.0	93.1	2.8	3
	6	16.6	1.30	3	394	--	84.1	--	1
1 Week	4	17.6	1.32	3	398	57.9	95.1	10.0	3
	6	18.7	1.44	3	404	--	97.9	--	1
3 Weeks	4	22.3	4.41	3	508	51.8	105.4	3.1	3
	6	23.9	5.74	3	540	--	107.6	--	1
12 Weeks	4	18.4	0.78	3	506	25.1	102.8	3.6	3
	6	18.9	0.86	3	370	24.4	92.4	2.0	2

Note: To convert Pascals to psi, multiply by 1.45×10^{-4}.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

PROGRAM CONCLUSIONS

1. Significant improvements in the anaerobic char yield at 800°C of unsaturated polyesters were achieved by this program. Conventional polyesters provide char yields of five percent or less whereas the developed unsaturated polyester provided char yields of 40+ percent. This prepolymer consisted of phthalic, fumaric and diphenic acids reacted with 2,7-naphthalene diol and 9,9-bis(4-hydroxyphenyl) fluorene.

2. Combinations of aromatic diacids and diols to produce vinyl-monomer-soluble prepolymers were developed. Thus, even though several aromatic polyester prepolymers produced good char yields, these prepolymers had very limited solubility in vinyl monomers. The use of the cross-planar diol, 9,9-bis(4-hydroxyphenyl)fluorene, which significantly lowered the crystallinity of the aromatic polyester prepolymers, provided prepolymers which were soluble in styrene up to 85 weight percent. These styrene soluble prepolymers were also very soluble in divinylbenzene, triallyl cyanurate, diallyl isophthalate and methylvinylpyridine.

3. None of the reactive monomers investigated was found capable of producing char at 800°C (N_2). However, the addition of char producing catalyst to monomers and/or prepolymers was not investigated extensively. Phosphorus compounds in some blends did show positive effects toward char production.

4. The developed homogeneous, unsaturated polyester blends were cured with radical catalysts used with conventional polyester systems. State-of-the-art processing was used to produce several graphite composites.

5. The graphite composites produced from the high char yield polyester had low shear strengths.

RECOMMENDATIONS

1. Efforts toward the development of a high char yield unsaturated polyester resin system should be continued. Graphite composites represent a single useful application for such a resin system. Conventional polyesters are used, however in a number of applications where increased fire resistance would be most welcomed.

2. The investigation of the developed polyesters' ability to produce high strength graphite composites must include resin-fiber compatibility studies. Resin modifications as well as use of wetting and coupling agents are expected lead to much improved composite strengths.

3. From its handling properties, the developed aromatic unsaturated polyester resin appears to be somewhat brittle. The investigation of flexiblizers such as propylene glycol in the polyester backbone needs investigation.

SECTION V
EXPERIMENTAL

2,6-Naphthoyl Chloride

21.6 Grams (0.10 mole) of 2,6-naphthalene dicarboxylic acid and 50 ml of thionyl chloride were placed in a dry 100 ml three neck round bottom flask equipped with a stirrer, thermometer, condenser, and dry nitrogen supply. Fifteen drops of pyridine were added and the reaction mixture was heated with stirring to gentle reflux (66^{o}-68^{o}C) for one hour. The excess thionyl chloride was stripped off under vacuum, and the reaction mixture taken up in 100 ml of boiling toluene. The hot toluene solution was filtered through a fiberglass plug and 20.4 grams (81 percent yield) of yellow needles were collected from the filtrate after cooling. The observed melting point was 179^{o}-182^{o}C (corrected) compared to a reported melting point of 182^{o}-5^{o}C (G.L. Driscoll, Chem. Abstracts 71:81024B).

Polyester Resin (P4)

3.8g (0.015 Mole) of 2,6-naphthoyl chloride and 2.3g (0.015 mole) of fumaryl chloride were dissolved in ten times their weight (61g) of dry tetrahydrofuran. This solution was shaken vigorously for five minutes with a solution consisting of: 4.0g (0.025 mole) of 2,7-naphthalene diol and 1.44g (0.01 mole) of 1-naphthol dissolved in ten times their weight of water (55g) containing an additional 10.5g of KCl (16 percent KCl solution) and 3.08g (0.077 mole) of NaOH. The weight of NaOH was slightly in excess. The prescribed quantity of NaOH was 1.1 times the equivalent of phenolic OH (0.066 mole). The reaction mixture exothermed to about 35^{o}C upon mixing of the solutions.

The reaction mixture was poured into 300 ml of water and filtered. The powdery precipitate was washed three times with water, followed by three washings with ethyl alcohol. The product was dried at 120°C under vacuum and yielded 6.3g (67 percent) of greyish tan powder.

p-Phenylene bis(magnesium bromide)

Magnesium turnings (3.65g, 0.15 mole) and 6 ml dry THF were placed in a 200 ml flask equipped with a stirer, condenser, addition funnel and dry nitrogen purge. p-Dibromobenzene (17.70g; 0.075 mole) was dissolved in 38 ml of dry THF and added dropwise from the additional funnel after a crystal of iodine had been added. After the addition was complete, 75 ml of dry THF was added and the reaction was refluxed overnight yielding a yellow solution and insoluble white product. The solution was removed with a filter stick and the residue was washed twice with 100 and 150 ml portions of hot dry THF followed by a wash with 50 ml of hexane. The product was transferred to an addition funnel with hexane for immediate use. The yield was approximately 8 grams (38 percent). Caution: The product is reported to be pyrophoric.

p-Phenylene-bis(phenylphosphonylchloride)

Approximately 40 grams of phenyl phosphonyl dichloride was distilled under vacuum into a dried reaction flask. The flask was equipped with a stirrer, addition funnel, condenser and dry nitrogen purge - 35 ml of hexane was added and approximately 8 grams of p-phenylene bis(magnesium bromide) dispersed in 70 ml of hexane was added over a period of one hour. Residual Grignard reagent was washed from the addition funnel with 100 ml of additional hexane (Note: frequent plugging).

A slight exotherm occurred during the addition and a yellow oil separated from the reaction mixture. After addition was complete the reaction was stirred for an additional two hours. The liquid was removed from the salts with a filter stick and washed with 50 ml of hexane. The combined liquids were distilled at atmospheric pressure to remove the solvent and finally under vacuum to remove excess phenylphosphonyl dichloride (BP 105°C) The product was a yellow liquid that darkened somewhat during the final stages

of phenylphosphonyl dichloride removal. On cooling, the product was a viscous glassy liquid. It weighed 12.5 grams (113 percent based on 8g of Grignard reagent).

100 Gram Prepolymer Synthesis (P16)

To a three liter flask equipped with an air powered stirrer, thermometers and addition funnels, was added 390g water, 570g tetrahydrofuran (THF) 167g, KCl, 37.7g 50 percent NaOH and 12.0g (0.075 mole) 2,7-naphthalene diol. The homogeneous mixture was cooled in an ice bath and 431 grams of ice was added. The contents of three addition funnels were then added rapidly with vigorous stirring. Funnel number one contained 10.2g (0.050 mole) phthaloyl chloride, 23.0g (0.150 mole) fumaryl chloride, 27.9g (0.100 mole) diphenoyl chloride and 122g THF. The second funnel contained 61.2g (0.175 mole) 9,9-bis(4-hydroxyphenyl)fluorene (BHPF) and 200g THF. The third funnel contained 28.8g water, 15.1g 50 percent NaOH and 14.4 (0.100 mole) 1-naphthol. The contents of funnel one were added at the same time as the contents of funnels two and three. The contents of funnel three were added immediately after funnel two was empty. All additions occurred in less than one minute. The funnels were then washed with 150 grams of THF and the washings added to the reaction mixture. The initial temperature of the completed mixture was $5^{o}C$. After 20 minutes of vigorous stirring, the temperature was $10^{o}C$ and mild warming with a hot water bath was started. When the temperature reached $30^{o}C$ (10 minutes) the reaction mixture was poured rapidly into 5ℓ of distilled water and a gummy precipitate formed rapidly. The liquid was decanted from the product and then washed twice with water, followed by two washings with isopropanol. The putty-like residue was dried in a vacuum oven for three hours at $120^{o}C$, ground and passed through a 30 mesh sieve, and redried in the vacuum oven for three hours. The resulting yellow-tan powder weighed 111.0g (87.4 percent of theory).

Typical Laminating Prodecure (Laminate #3)

Laminate Resin:	Parts by Weight
Polyester Prepolymer	100
Triallyl cyanurate	3
Styrene	30

Laminate Resin:	Parts by Weight
USP 245 (2,5-dimethyl-2,5-bis(2-ethyl-hexanoylperoxy)hexane	1.33
Luperox 500T (Dicumylperoxide) (Tech)	1.33

Reinforcement:

Union Carbide Thornel 300 fiber, Grade WYP 30 1/0, UC-309 size, zero twist.

Apply a nominal nine mil coating to Mylar (3 mil) fiber using a hot melt coater set at 150°F (12 mil gap). Overwrap the resin coating with the reinforcement fiber. Impregnate the fibers using vacuum table with squeegee at 150°F. The areal weights of the resin and fiber are respectively 139 and 186 g/m^2. The prepreg at this stage is leathery and separates from the Mylar without difficulty.

Fifteen plies of 4" x 4" prepreg are layed up in a trap mold between layers of porous Teflon coated glass and two bleeder plies of Style 120 glass cloth. Vacuum pressure is applied to the part and the mold is placed into an RT press under contact pressure only. The press is turned and set at 350°F. When the resin thickens 50 psi was applied for Laminate #3. This was after one hour and the temperature was 195°F. When the part reaches 350°F (2¼ hours), hold the temperature at 350°F for one hour.

The resulting composite had 64 volume percent fiber and 3.1 volume percent voids, with an average thickness of 0.0995 inch.

REFERENCES

1. P.M. Morgan, "Aromatic Polyesters with Large Cross-Planar Substituents" Macromolecules, Vol. 3, No. 5, September-October 1970, page 536.

2. A.J. Conix and U.L. Laridor, "Production of Linear Aromatic Polyesters" U.S. Patent 3,028,364, April 1962.

3. A.J. Conix, "Production of Linear Aromatic Polyesters Containing Isophthalic Acid", U.S. Patent 3,216,970, November 1965.

4. W.A. Hare, "Direct Solution Preparation of Aromatic Polyesters", U.S. Patent 3,234,168, February 1966.

5. R.J. Thomas, "Polyesters Prepared from Bisphenols and Isopropylidene Bis(p-Phenylene-oxy) Diacetyl Chloride", U.S. Patent 3,828,066, August 1974.

6. W.W. Howerton, "Polyesters of 4,4'-Hexafluoroisopropylindene Diphenol", U.S. Patent 3,824,211, July 1974.

7. L.B. Sokolov and V. Kudim, "Method for Preparing Aromatic Polyesters", U.S. Patent 3,933,713, January 1976.

8. Y. Aito, et. al., "A Thermally Stable Diallyl Naphthalate Resin", 30th Society of the Plastics Industry Conference, 1975, Paper 19E.

9. J. Brandrup and E. Immergut, "Polymer Handbook", 1st and 2nd editions, John Wiley & Sons.

10. B. Vollmert, "Polymer Chemistry", Springer-Verlay, New York, 1973, page 137-147.

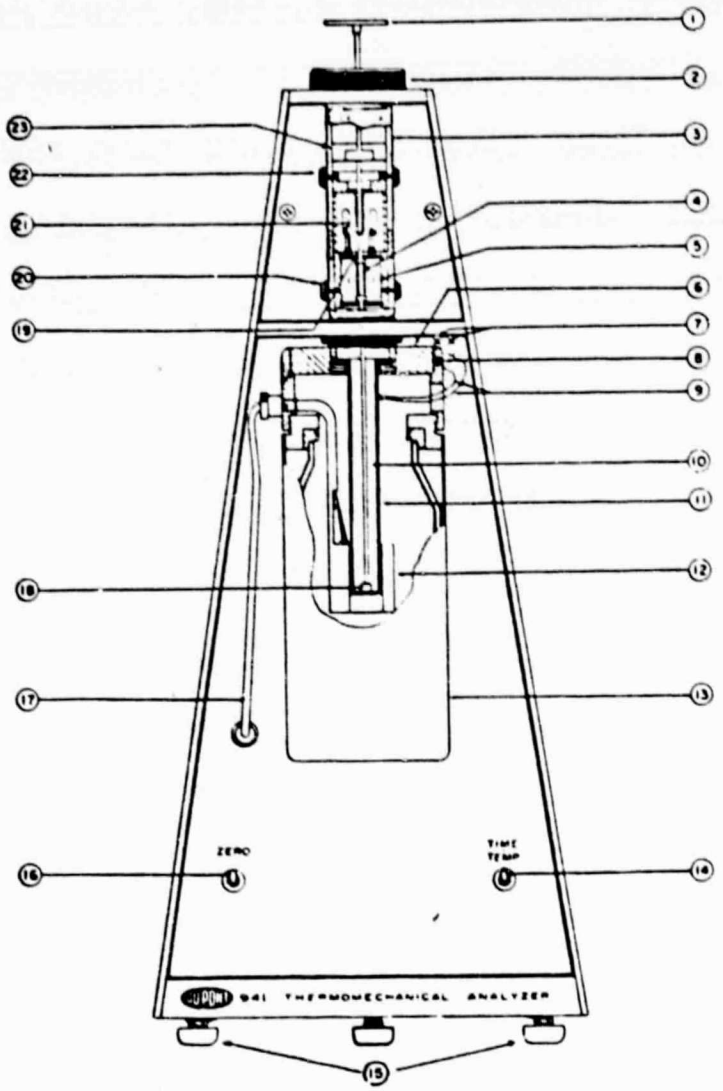
APPENDIX A
DISTORTION TEMPERATURE UNDER LOAD

Distortion temperature under load (DTUL) is carried out on a small cured sample of resin with essentially parallel faces as sketched in Figure A-1. The intercept of the expansion curve with the softening curve (or a decrease in slope of the expansion curve) is taken as the temperature at which the sample will no longer support the compressive load placed upon it.

DTUL experiments are conducted using a 0.635 mm (0.025 inch) diameter flat bottom probe that has a 100g load perpendicular to the test surface. This places a 3.1 MPa (449 psi) stress on the sample. Heating rates are at 15^{o}C/minute.

The suggested performance temperature is 50^{o}C below the DTUL temperature for extended service.

SKETCH OF SET-UP TO DETERMINE DISTORTION TEMPERATURE UNDER LOAD (DTUL)



Item	Description	Item	Description
1	Weight tray	12	Heater assembly
2	Retainer nut	13	Dewar
3	Head assembly	14	Time-Temp. switch
4	LVDT core	15	Adjustable legs
5	LVDT	16	Zero switch
6	Dewar cap	17	Heater lead wire
7	Thermocouple connectors	18	Sample
8	Set screws	19	Shaft assembly (upper)
9	Thermocouple wires	20	Transducer Position control
10	Shaft assembly (lower)	21	Zero spring
11	Sample holder tube	22	Probe Position control
		23	Upper Bearing guide

Figure 19.

APPENDIX B
C-SCAN OF POLYESTER-CARBON FIBER COMPOSITES

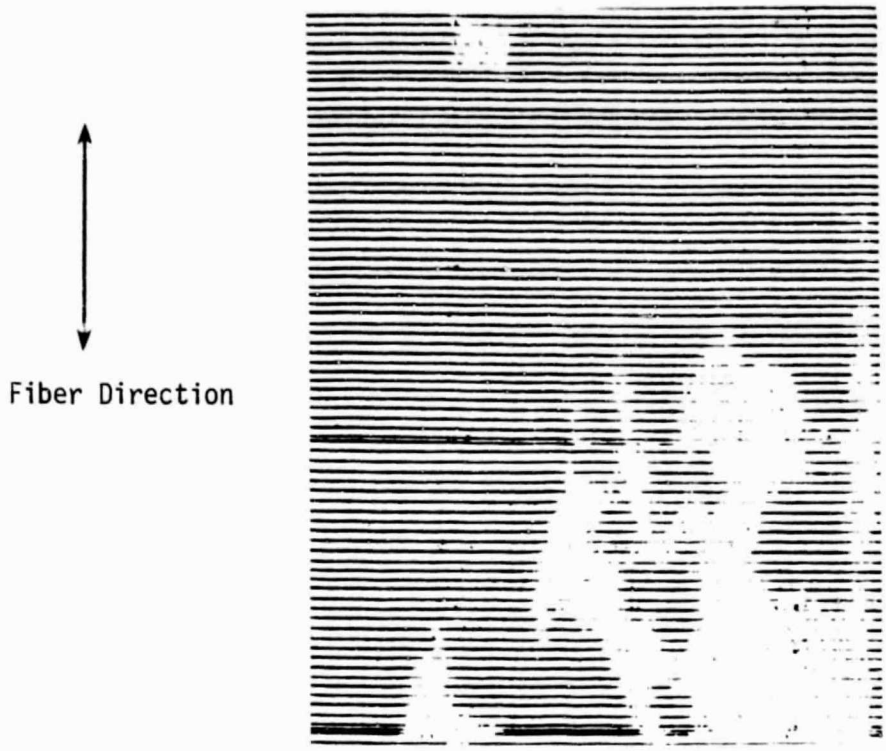


Figure B1A. C-scan of carbon fiber reinforced polyester Laminate #1 at low sensitivity.

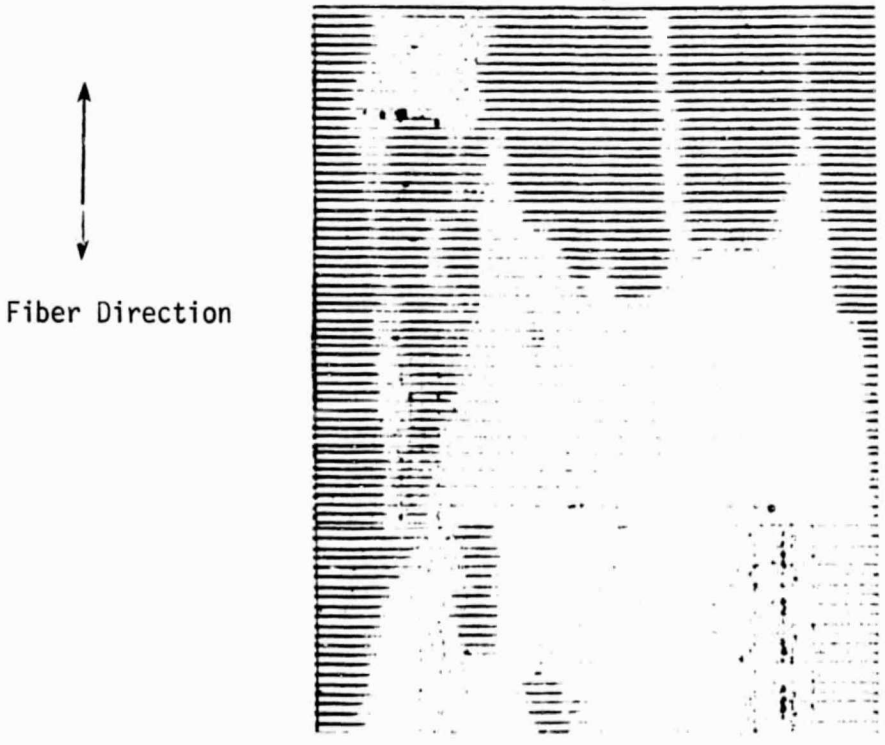


Figure B1B. C-scan of carbon fiber reinforced polyester Laminate #1 at high sensitivity.

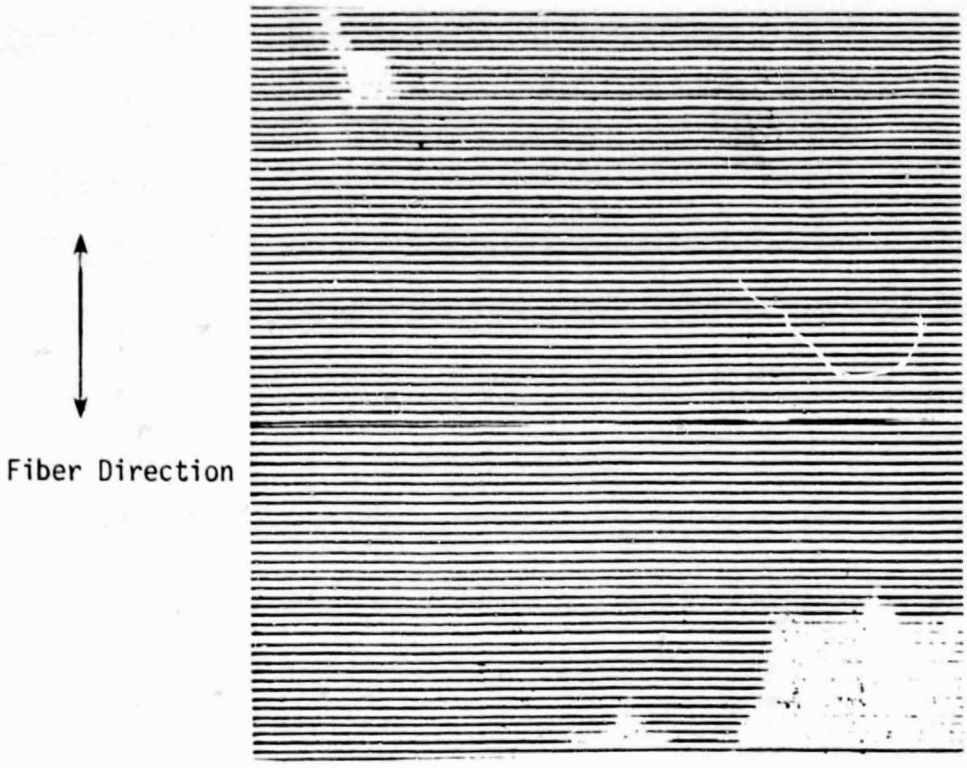


Figure B2A. C-scan of carbon fiber reinforced polyester Laminate #2 at low sensitivity.

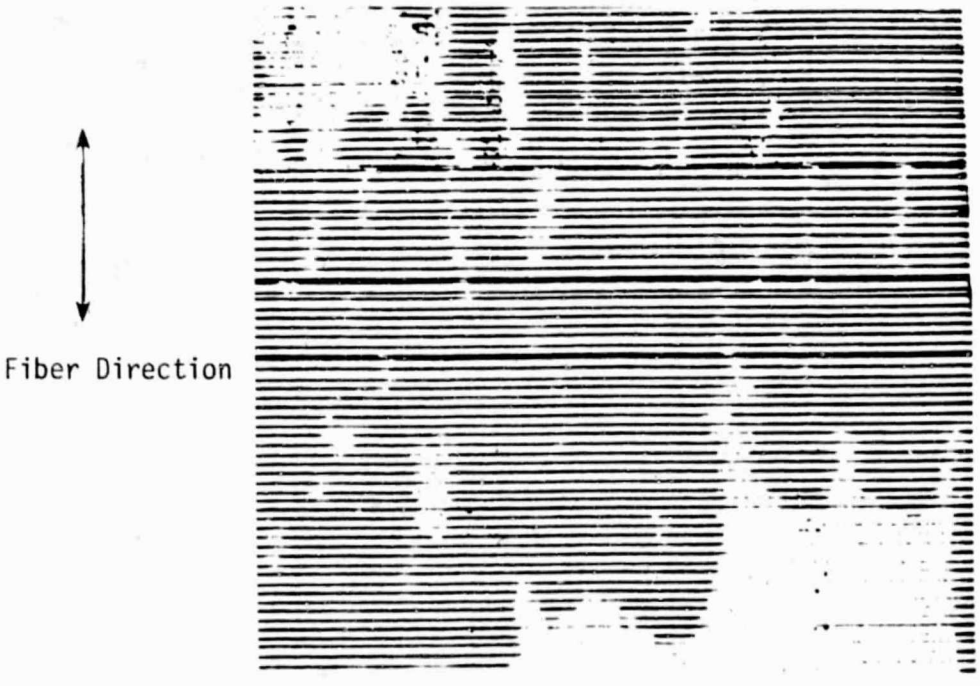


Figure B2B. C-scan of carbon fiber reinforced polyester Laminate #2 at high sensitivity.

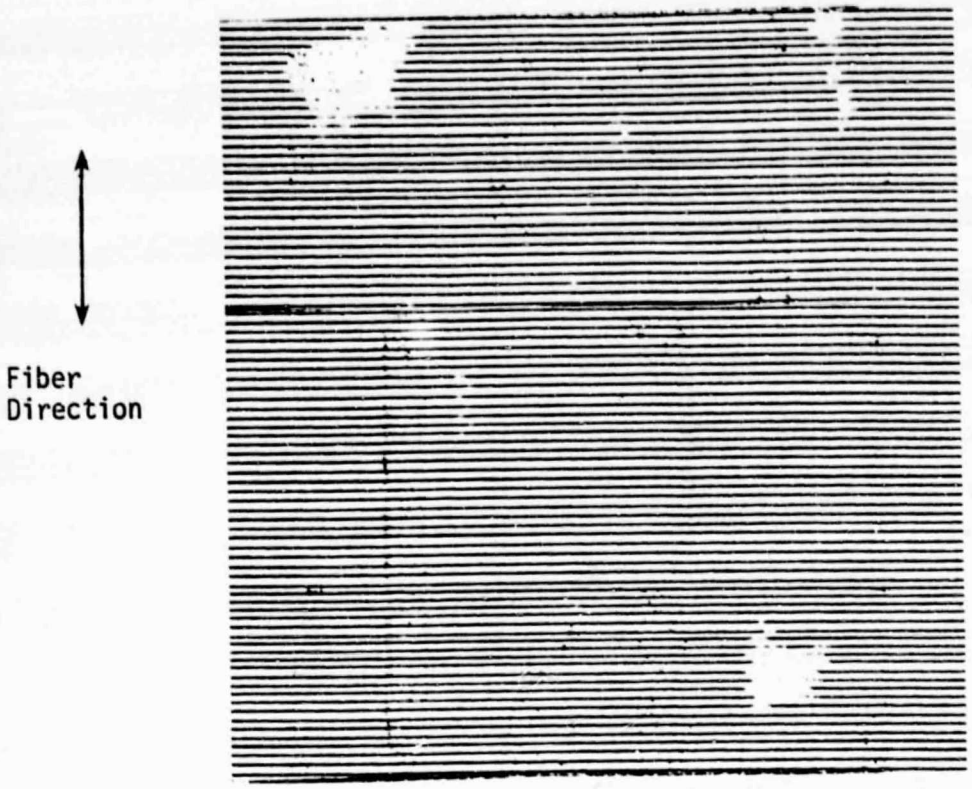


Figure B3A. C-scan of carbon fiber reinforced polyester Laminate #3 at low sensitivity.

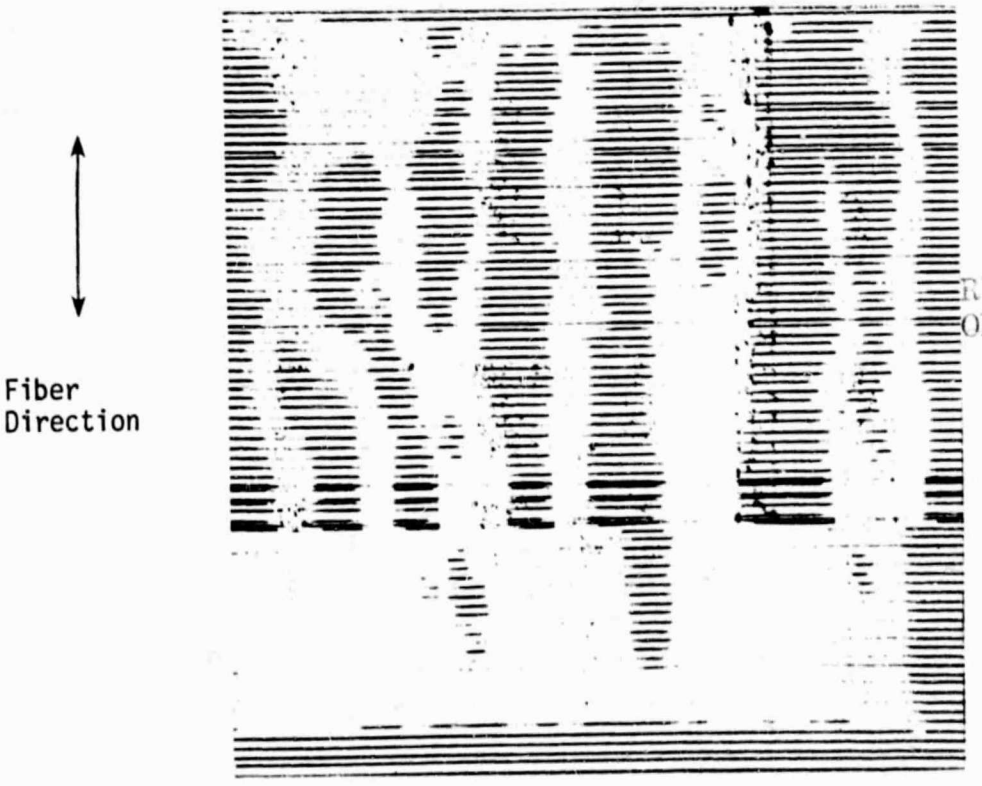


Figure B3B. C-scan of carbon fiber reinforced polyester Laminate #3 at high sensitivity.

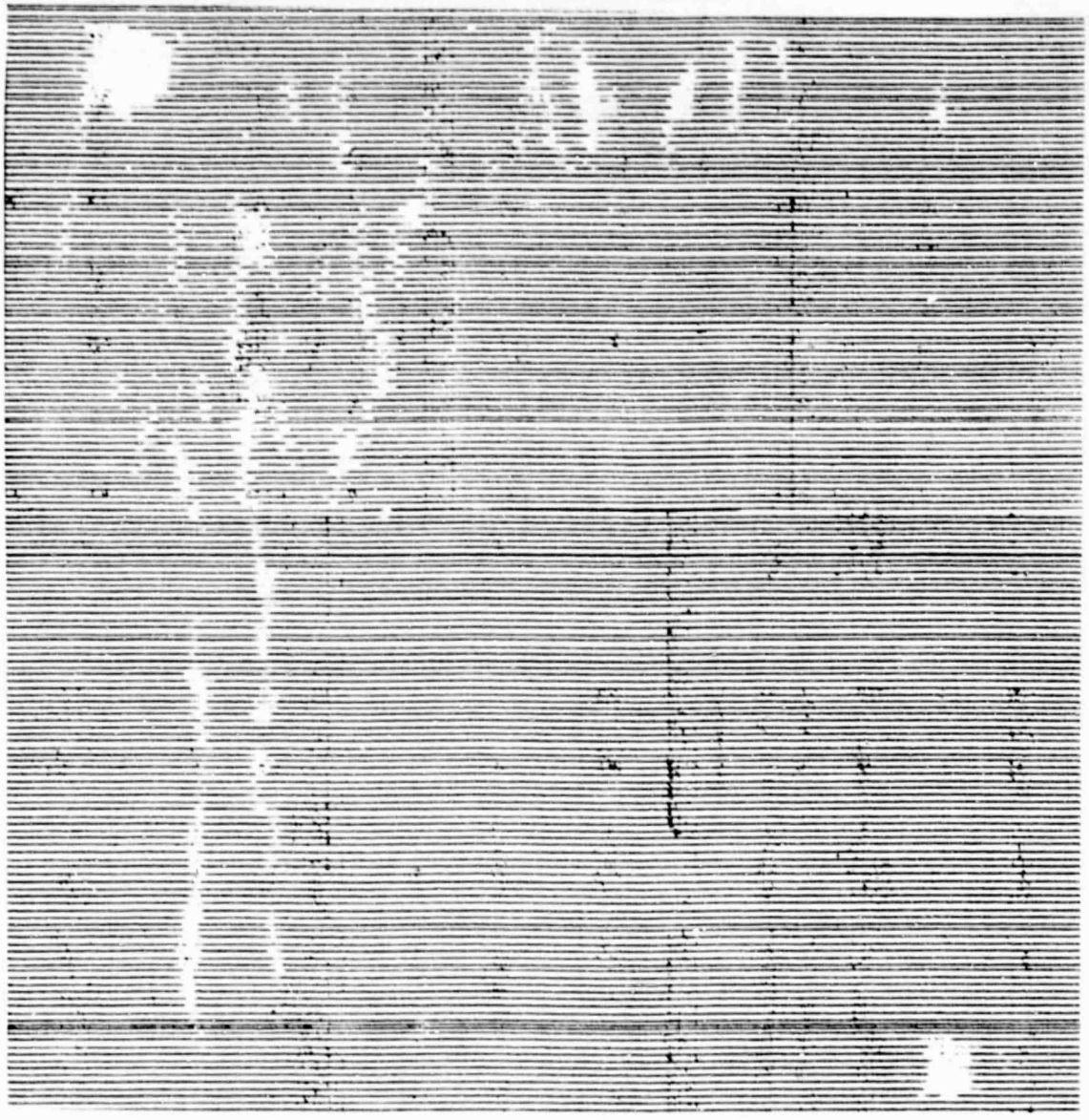
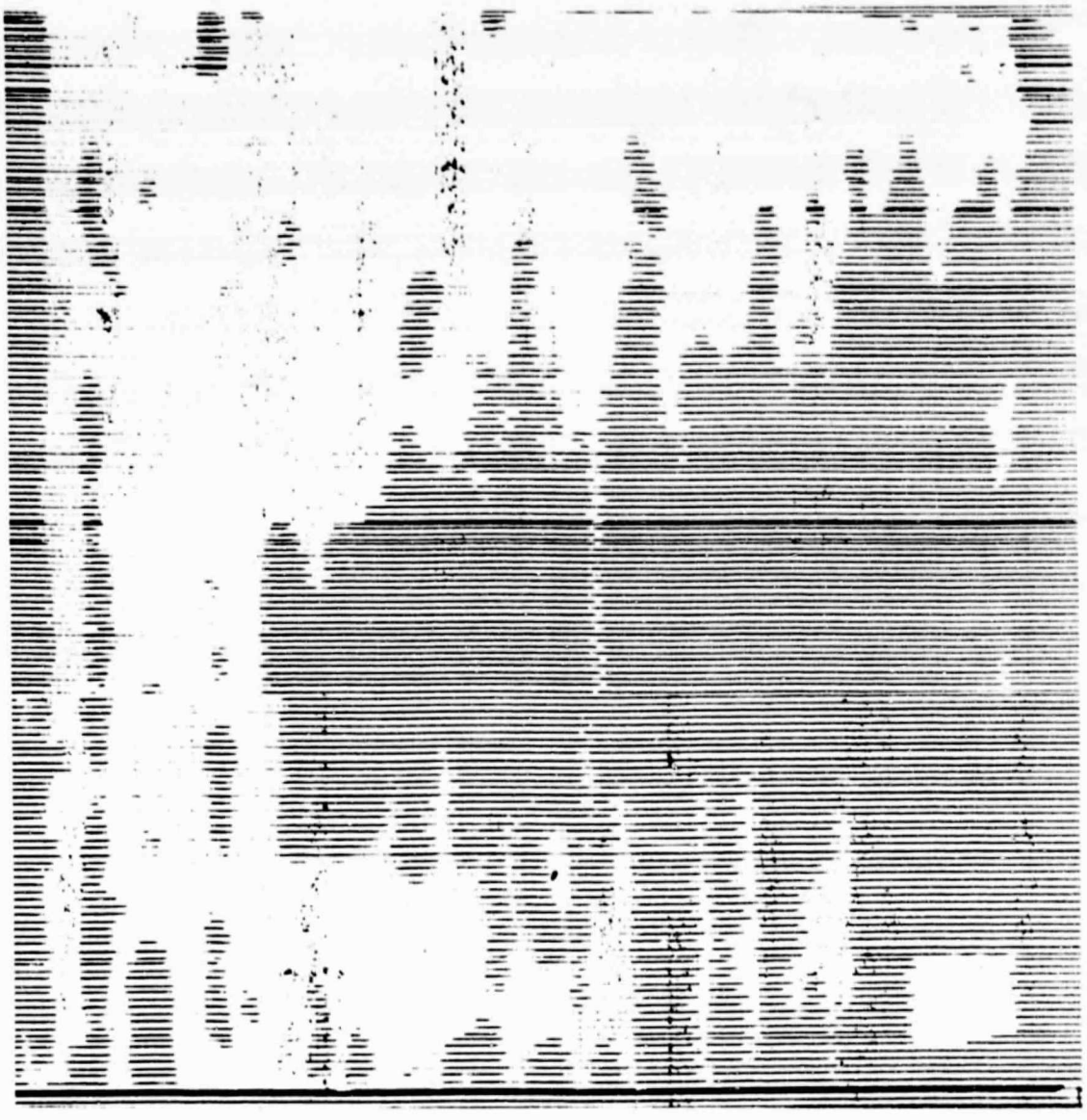
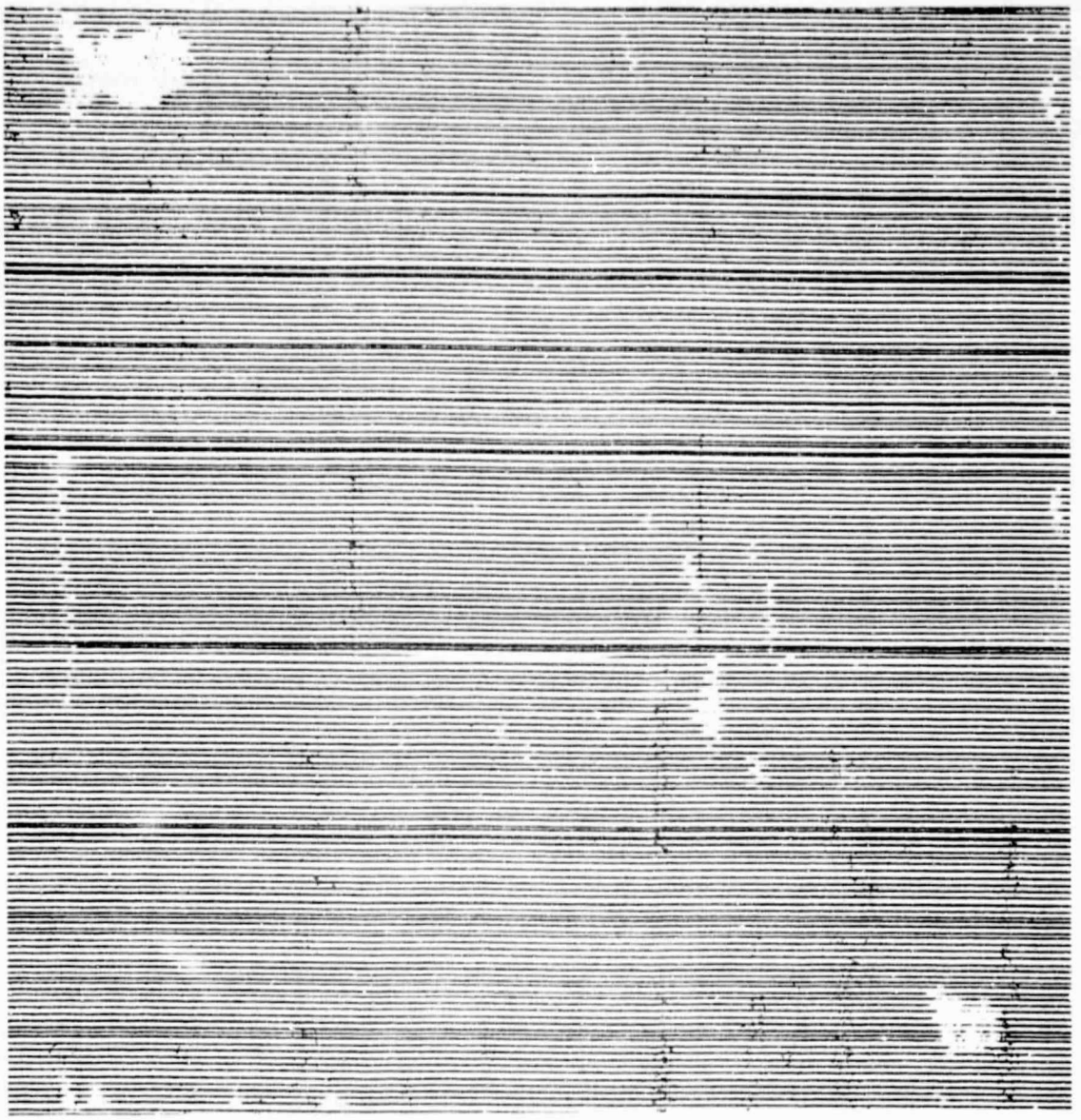


Figure B4A. C-scan of carbon fiber reinforced polyester Laminate #4 at low sensitivity.
(Reduced 77%)



Fiber
Direction

Figure B4B. C-scan of carbon fiber reinforced polyester Laminate #4 at high sensitivity.
(Reduced 77%)



Fiber
Direction

Figure B5A. C-scan of carbon fiber reinforced polyester Laminate #5 at low sensitivity.

(Reduced 77%)

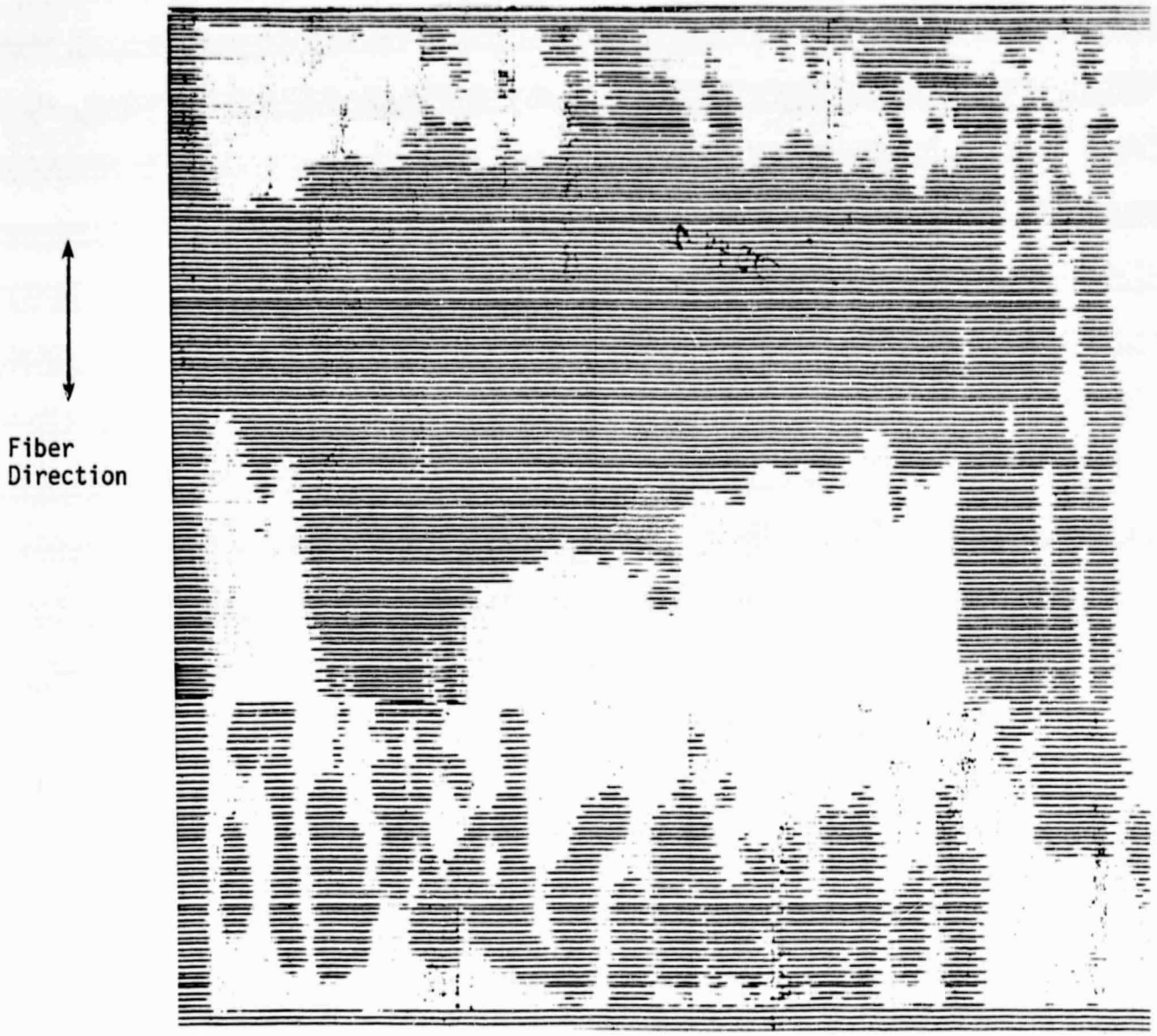
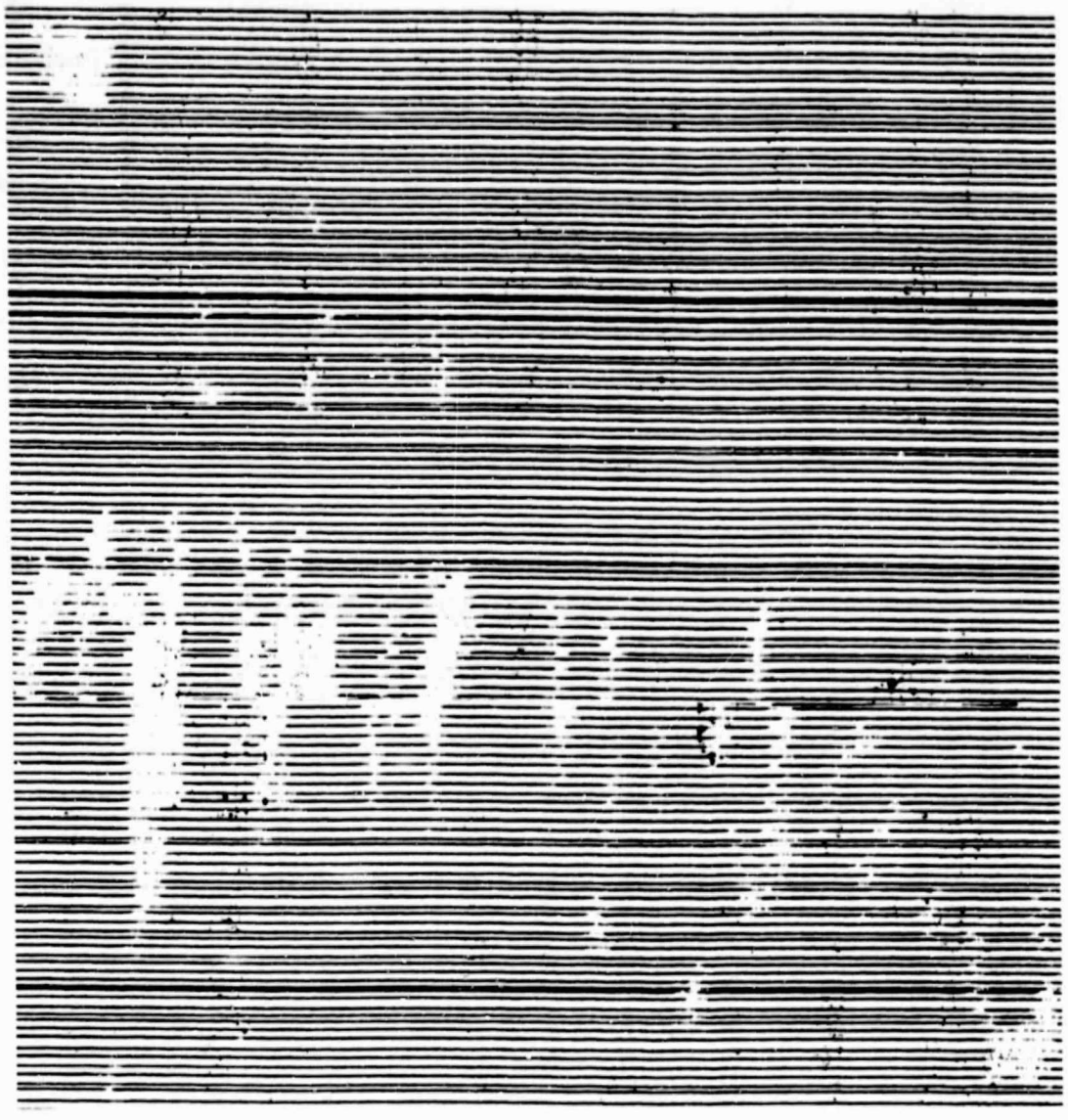


Figure B5B. C-scan of carbon fiber reinforced polyester Laminate #5 at high sensitivity.

(Reduced 77%)



Fiber
Direction

Figure B6A. C-scan of carbon fiber reinforced polyester Laminate #6 at low sensitivity.

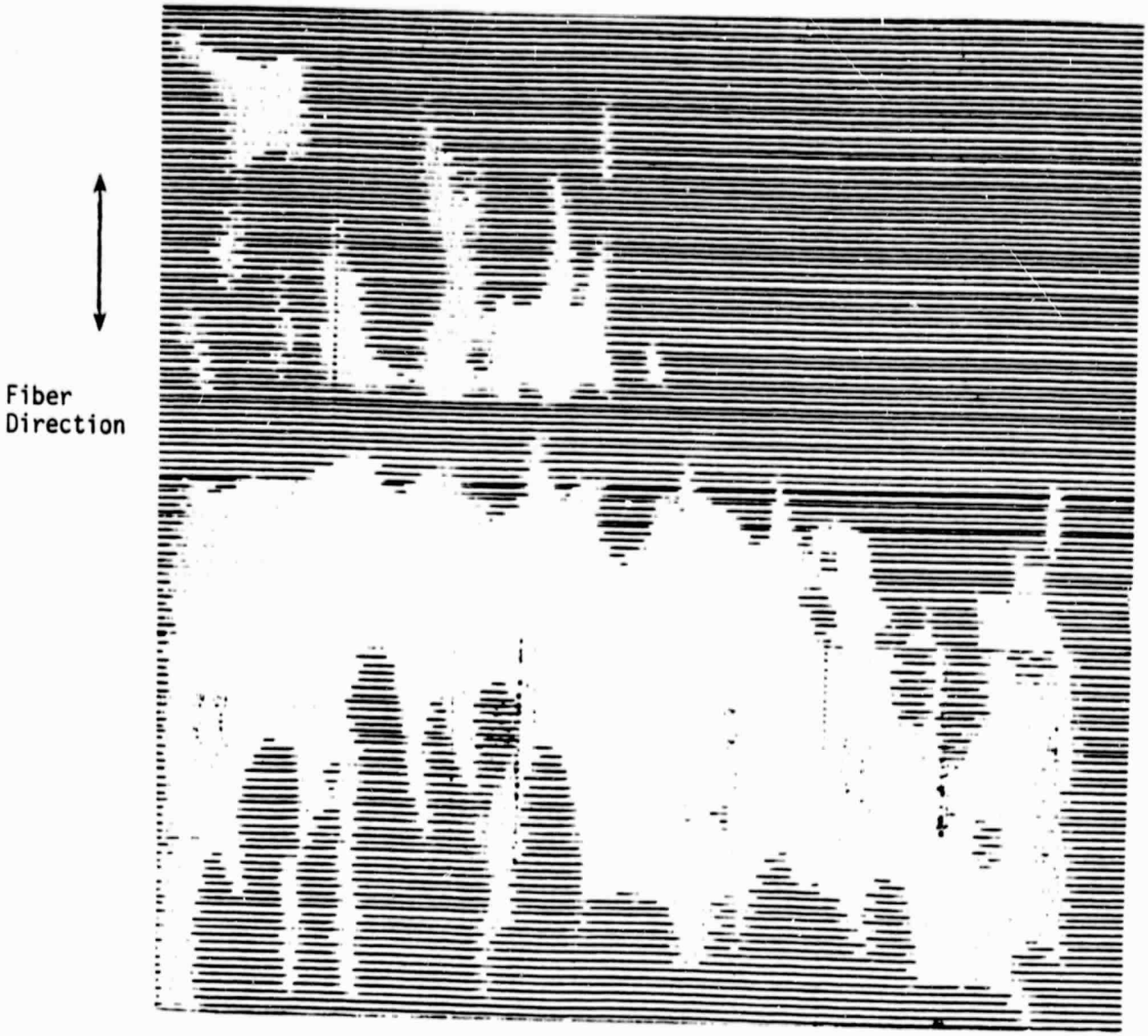


Figure B6B. C-scan of carbon fiber reinforced polyester Laminate #6 at high sensitivity.

APPENDIX C
ABBREVIATIONS

500T	Dicumyl Peroxide
BHPF	9,9-bis(4-hydroxyphenyl)fluorene
BZP	Benzoyl Peroxide
CHP	Cumene Hydroperoxide
DHN	Dihydroxy Naphthalene
DTUL	Distortion Temperature Under Load
DVB	Divinyl Benzene
MEKP	Methylethylketone Peroxide
MVP	2-Methyl-4-Vinylpyridine
NDCA	2,6-Naphthalene Dicarboxylic Acid
PA	Phthalic Acid
PBW	Parts by Weight
PPDC	Phenylphosphonyl Dichloride
PPPC	p-Phenylene di(phenylphosphonyl chloride)
TAC	Triallylcyanurate
TGA	Thermogravmetric Analysis
THF	Tetrahydrofuran
VBP	4-Vinylbiphenyl
Y_c^{800}	Char yield at 800^{o}C