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Polyphenyl-as-triazines

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Polyphenyl-as-triazines*

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SUMMARY

High molecular weight soluble polyphenyl-as-triazines were prepared at ambient temperature in m-cresol by the cyclopolycondensation of 2,6-pyridinediyl dihydrazidine (diamidrazone) with various aromatic dibenzil type reactants. Clear lemon yellow films, which exhibited good toughness and flexibility, were cast from solution. The isolated yellow polymers readily formed clear yellow to orange solutions in chloroform or sym-tetrachloroethane at concentrations as high as 30% solids. By TGA, polyphenyl-as-triazines exhibited a two-stage decomposition, commencing at ~400°C, in both air and nitrogen. The polymers exhibited excellent stability at 260°C (500°F) in air, but at 290°C (554°F) significant weight losses occurred. Initial evaluation as an adhesive and resin matrix in Morganite I composites demonstrated the potential of polyphenyl-as-triazines as structural resins. Prior to polymer work, a series of model compounds were prepared and characterized.

INTRODUCTION

High molecular weight soluble poly-as-triazines [1] were recently prepared by the cyclopolycondensation of 2,6-pyridinediyl dihydrazidine

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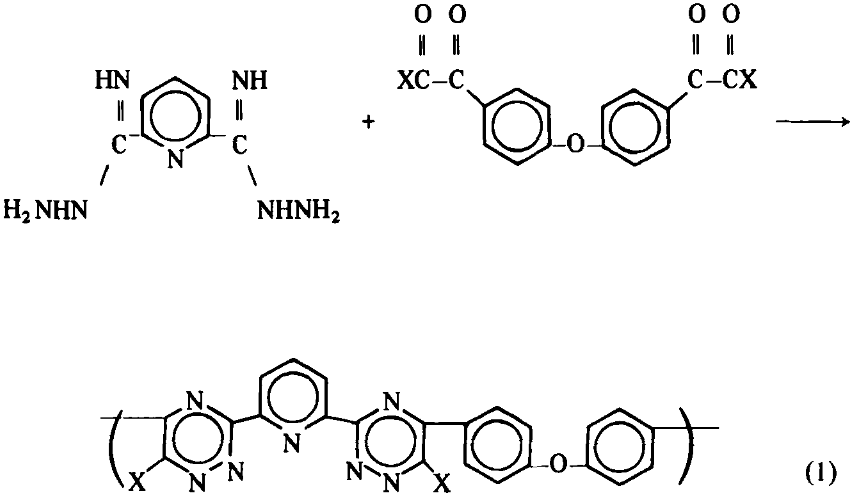
(diamidrazone) with p,p-oxybis(phenyleneglyoxal hydrate) and with p,p′-oxydibenzil as shown in Eq. (1).



(1)

where X = H or C_6H_5.

The work presented in this paper is an extension of earlier work and was performed principally to determine the effect of polymer structure on certain physical properties, such as glass transition temperature (T_g) and solubility, and to demonstrate the potential of polyphenyl-as-triazines as useful structural resins.

EXPERIMENTAL

Reactants

2-Pyridyl hydrazidine was prepared for model compound work following the procedure of Case [2] and obtained as white needles, mp 95-96°C (lit [2] mp 95-96°C).

2,6-Pyridinediyl dihydrazidine was prepared as previously described [1] by the addition of hydrazine to 2,6-dicyanopyridine in ethanol to provide a white solid, mp 230-231°C (dec) (lit [1] mp 230-231°C dec).

Para- and meta-bis(phenylglyoxaloyl)benzene were prepared by the reaction of the diacid chloride of the appropriate phenylenediacetic acid with benzene and anhydrous aluminum chloride followed by oxidation of the resulting intermediate with selenium dioxide in acetic acid.

The other dibenzil type reactants were synthesized as previously described [1] through the reaction of the appropriate arylene compound with phenylacetyl chloride and anhydrous aluminum chloride in methylene chloride. The resulting intermediates were oxidized to the corresponding dibenzils with selenium dioxide in acetic acid. To obtain p,p'-carbonyldibenzil, p,p'-methylenedibenzil was oxidized under pressure in a bomb at 230°C with selenious acid. The dibenzils are shown in Table 1.

Model Compounds

The model compounds were prepared in essentially quantitative yields by refluxing stoichiometric quantities of 2-pyridyl hydrazidine with the dibenzil in solvents such as benzene, ethanol, or m-cresol. The following procedure is representative of model compound formation.

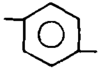
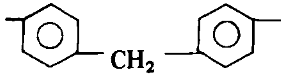
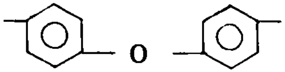
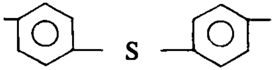
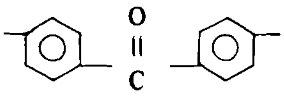
p,p'-Bis{6-[3(2-pyridyl)-5-phenyl-as-triazinyl]}benzophenone. p,p'-Carbonyldibenzil (0.8928 g, 2.0 mmole) was added to a solution of 2-pyridyl hydrazidine (0.5448 g, 4.0 mmole) in benzene (40 ml). The resulting yellow solution was stirred at ambient temperature for 5 min followed by heating to the reflux temperature and allowing the solvent to distill off to a residual volume of ~8 ml. The yellow residue was concentrated to dryness in vacuo at 100°C to provide a yellow solid (1.26 g, 98% yield), mp 153-155°C. Further drying at 78°C in vacuo over phosphorus pentoxide raised the mp to 154-155.5°C. Characterization of p,p'-bis{6-[3(2-pyridyl)-5-phenyl-as-triazinyl]}benzophenone is given in Table 2.

Polymers

All polymers were prepared by solution polymerization in m-cresol at 20% solids content. The following procedure is representative of polymer preparation.

Poly[3,3'-(2",6"-pyridinediyl)-6,6'-(p,p'-carbonyldiphenylene)di(5-phenyl-as-triazine)]. p,p'-Carbonyldibenzil (4.4643 g, 0.010 mole) was added to a solution of 2,6-pyridinediyl dihydrazidine (1,9322 g, 0.010 mole) in m-cresol (25.6 ml) at ambient temperature. After stirring for 0.5 hr at ambient temperature, a portion of the viscous yellow solution was poured into methanol in a Waring Blendor to precipitate a fibrous yellow solid. The yellow solid was thoroughly washed with methanol and dried for 4 hr at 150°C in vacuo. The resulting intermediate yellow polymer exhibited a polymer softening temperature of 300-309°C and an inherent viscosity (η_{inh}, 0.5% H_2SO_4 at 25°C) of 0.74.

Table 1. Dibenzils

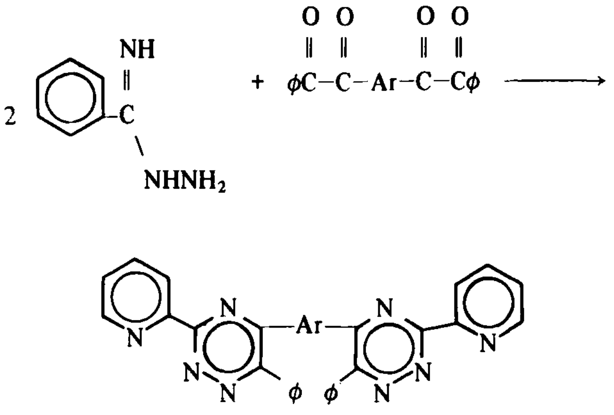
$H_5C_6OCOC{-}Ar{-}COCOC_6H_5$ Ar =	Mp, °C	Lit mp, °C	Formula	Elemental analysis[a] % C	 % H
	125-126	125-126[3]	$C_{22}H_{14}O_4$	–	–
	98-99	98-99.5[4]	$C_{22}H_{14}O_4$	77.24 (77.18)	4.17 (4.12)
	141.5-143	144-144.5[5]	$C_{29}H_{20}O_4$	86.24 (86.11)	6.11 (5.98)
	105-106	106.4-107.4[5]	$C_{28}H_{18}O_5$	–	–
	91-92.5	90-91.6[5]	$C_{28}H_{18}O_4S$	–	–
	128-130	–	$C_{29}H_{18}O_5$	78.26 (78.02)	4.13 (4.06)

[a] Theoretical values reported in parenthesis.

The remaining m-cresol solution was placed under a nitrogen atmosphere and refluxed (200°C) for 1 hr. The final polymer was isolated by pouring the viscous yellow m-cresol solution into methanol in a Waring Blendor followed by thorough washing with methanol and drying for 4 hr at 150°C in vacuo. The η_{inh} of the final polymer was 1.23. Additional characterization is given in Tables 3 and 4.

DISCUSSION

Prior to polymer synthesis, a series of model compounds were prepared in essentially quantitative yields from the reaction of various dibenzils as shown in Table 1 with 2-pyridyl hydrazidine as shown in Eq. (2).

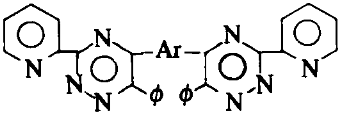
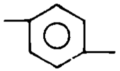
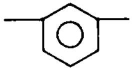
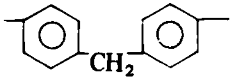


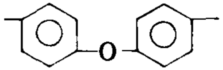
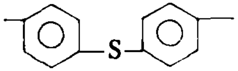
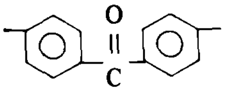
(2)

Ar = arylene

Although Eq. (2) indicates the formation of a single isomer with the phenyl groups in the 6,6′-position, the formation of other isomers is possible. For example, different isomers would be expected from the reaction of 2-pyridyl hydrazidine with p,p′-oxydibenzil and with p-bis(phenylglyoxaloyl) benzene since the carbonyl groups adjacent to the arylene moiety differs electromerically in reactivity from the carbonyl groups adjacent to the phenyl groups. The phenyl groups in the model compounds would be expected to be located predominantly in the 6,6′- and 5,5′-position, respectively, from p,p′-oxydibenzil and p-bis(phenylglyoxaloyl)benzene as indicated in Eq. (3).

Table 2. Phenyl-as-Triazine Model Compounds

 Ar =	Mp, °C	Formula	Elemental analysis[a]			Ultraviolet spectrum[b]	
			% C	% H	% N	λ_{max}, mμ	$\epsilon \times 10^{-3}$
	314-316	$C_{34}H_{22}N_8$	75.48 (75.26)	4.27 (4.09)	20.64 (20.65)	235 (S) 298 346	21.7 38.3 26.5
	265-267	$C_{34}H_{22}N_8$	74.97 (75.26)	4.04 (4.09)	20.68 (20.65)	234 (S) 292 343	23.9 42.9 26.3
	138-139	$C_{41}H_{28}N_8$	77.75 (77.83)	4.18 (4.46)	17.59 (17.71)	234 (S) 291 314 386	28.2 32.0 34.6 25.6

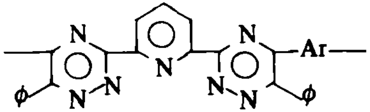
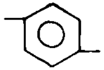
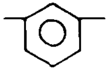
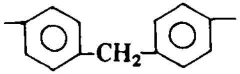
	141-142[c]	$C_{40}H_{26}N_8O$	75.72 (75.70)	4.11 (4.13)	17.54 (17.65)	237 (S) 318	26.7 25.7
	153-154.5	$C_{40}H_{26}N_8S$	73.65 (73.83)	4.01 (4.03)	17.04 (17.22)	233 (S) 289 332	28.3 42.3 25.7
	154-155.5	$C_{41}H_{26}N_8$	76.07 (76.14)	4.07 (4.05)	17.17 (17.33)	233 (S) 299 344	25.0 50.4 39.8

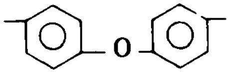
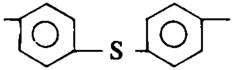
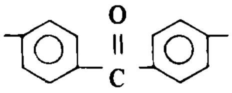
[a] Theoretical values reported in parenthesis.

[b] Determined in sulfuric acid, S refers to shoulder.

[c] Literature mp 142-143.5°C [1].

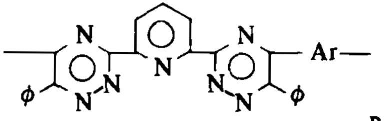
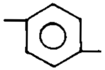
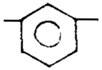
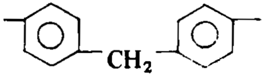
Table 3. Polyphenyl-as-triazines

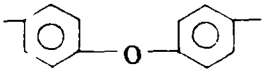
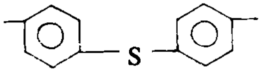
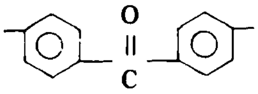
 Ar =	Polymer No.	Intermediate polymer[a]		Final polymer[b]						
						Elemental analysis			Ultraviolet spectra[f]	
		PST, °C[c]	η_{inh}, dl/g[d]	η_{inh}, dl/g[d]	Formula	% C	% H	% N	λ_{max}, mμ	$\epsilon \times 10^{-3}$
	IP	320-329	0.92	1.32	$(C_{29}H_{17}N_7)_n$	75.87	2.83	21.27	224 (S)	36.1
						(75.80)	(2.85)	(21.34)	334	28.3
	IIP	287-296	0.84	1.27	$(C_{29}H_{17}N_7)_n$	75.64	2.81	21.29	227	39.9
						(75.80)	(2.85)	(21.34)	333	31.3
	IIIP	270-280	0.65	1.18	$(C_{36}H_{23}N_7)_n$	77.98	4.15	17.65	219 (S)	44.9
						(78.10)	(4.19)	(17.71)	258	19.9
									333	27.4

 [g]	IVP	278-287	0.85	1.25	$(C_{35}H_{21}N_7O)_n$	75.76 (75.66)	3.79 (3.81)	17.52 (17.65)	222 (S) 271 335	46.4 20.6 25.6
	VP	282-290	0.77	1.19	$(C_{35}H_{21}N_7S)_n$	73.61 (73.53)	3.67 (3.70)	17.11 (17.16)	223 (S) 312	43.5 27.2
	VIP	300-309	0.74	1.23	$(C_{36}H_{21}N_7O)_n$	76.04 (76.17)	3.71 (3.73)	17.19 (17.28)	346	42.0

[a] After 0.5 hr in m-cresol at ambient temperature, dried 4 hr at 150°C in vacuo.
[b] After refluxing in m-cresol under nitrogen for 1 hr, dried as above.
[c] Polymer softening temperature.
[d] 0.5% H_2SO_4 at 25°C.
[e] Theoretical values reported in parenthesis.
[f] Determined in sulfuric acid, S refers to shoulder.
[g] Polymer previously reported [1].

Table 4. Thermal Properties of Polyphenyl-as-triazines

 Ar =	Polymer		Thermogravimetric analysis[b]						Isothermal weight loss, %			
			Air			Nitrogen			260°C (500°F)		290°C (554°F)	
	No.	T_g, °C[a]	T_1, °C[c]	T_2, °C[d]	T_3, °C[e]	T_1, °C[c]	T_2, °C[d]	T_3, °C[e]	100 hr	200 hr	50 hr	150 hr
	IP	260	395	405	538	370	395	560	1.0	1.1	22.8	58.6
	IIP	–	390	410	540	375	390	555	1.1	1.3	23.8	59.4
	IIIP	205	320	350	550	320	362	545	1.4	1.5	35.8	73.7

	IVP	223	380	420	535	355	390	540	0.9	1.2	24.5	74.1
	VP	–	380	415	533	360	395	565	1.3	1.4	13.2	71.9
	VIP	–	385	410	540	365	388	550	0.8	1.1	18.6	61.3

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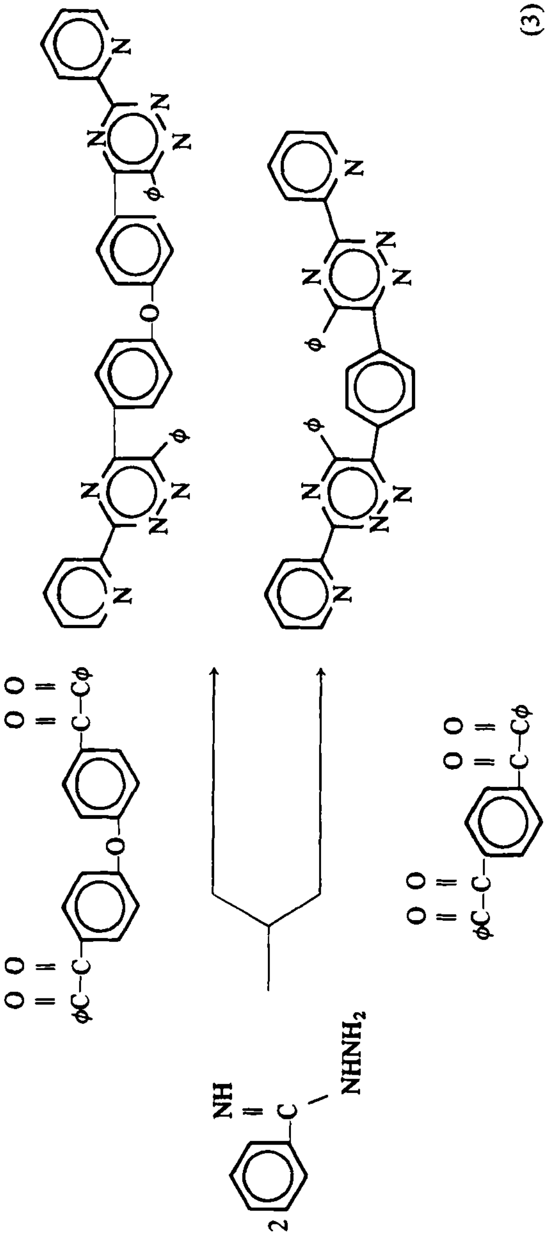
[a] Glass transition temperature, determined by dielectric loss measurements in vacuo at $\Delta T = 10°C/min$ and 1 kHz.
[b] Determined using a Dupont 950 thermalgravimetric analyzer at $\Delta T = 6°C/min$.
[c] T_1 = temperature of initial weight loss.
[d] T_2 = polymer decomposition temperature of initial break (see Fig. 2).
[e] T_3 = temperature of second break (see Fig. 2).



(3)

Characterization of the model compounds is given in Table 2. The UV spectra of the model compounds in sulfuric acid showed common absorptions at 235 ± 2 mμ and 294 ± 6 mμ, apparently associated with the as-triazine ring. The effect of the increase in length of the conjugated system is apparent in observing the λ_{max} of the p-phenylene versus the m-phenylene model compounds. The major λ_{max} occurs at 298 mμ for the p-phenylene model compound and at 292 mμ for the m-phenylene model compound.

Polymers were prepared from the reaction of stoichiometric quantities of 2,6-pyridinediyl dihydrazidine with various dibenzils in m-cresol at 20% solids content. At ambient temperature, clear yellow to light orange viscous solutions formed in <0.5 hr. Clear lemon yellow films cast from these solutions exhibited good toughness and flexibility. The polymer was isolated from solution by quenching with methanol in a Waring Blendor to provide a light yellow fibrous solid. Characterization of the intermediate polymers after drying for 4 hr at 150°C in vacuo is given in Table 3. The polymer softening temperature reflects the thermoplastic nature of these polymers and also is indicative of their good processability. The intermediate polymers were advanced to final polymers by heating their m-cresol solutions at the reflux temperature for 1 hr under nitrogen. Although the final polymers were of relatively high molecular weights, e.g., $\eta_{inh} = 1.3$ dl/g (Table 3), they exhibited solubility characteristics unique for all aromatic heterocyclic polymers. The polymers readily formed clear yellow to orange viscous solutions at concentrations as high as 30% solids content in chloroform or sym-tetrachloroethane. In a mixture of toluene and m-cresol (4:1), the polymers readily formed clear solutions at concentration as high as 20% solids content. In solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, or N-methylpyrrolidone, the polyphenyl-as-triazines failed to form clear solution at solids content as low as 1%.

Thermal Properties

The thermal properties of the final polymers are presented in Table 4. The T_g's were determined by dielectric loss measurements at a heating rate of 10°C/min and a frequency sweep of 100 to 1000 Hz on films cast from m-cresol solutions and dried at 150°C in vacuo for 4 hr. The polymer films were cycled in the dielectric test apparatus to 250°C in vacuo to remove residual solvent prior to a T_g determination. A typical dielectric loss spectrum is shown in Fig. 1 for Polymer IVP. The T_g was taken as the temperature at the intercept of the temperature versus dissipation factor curve at 1 Kc.

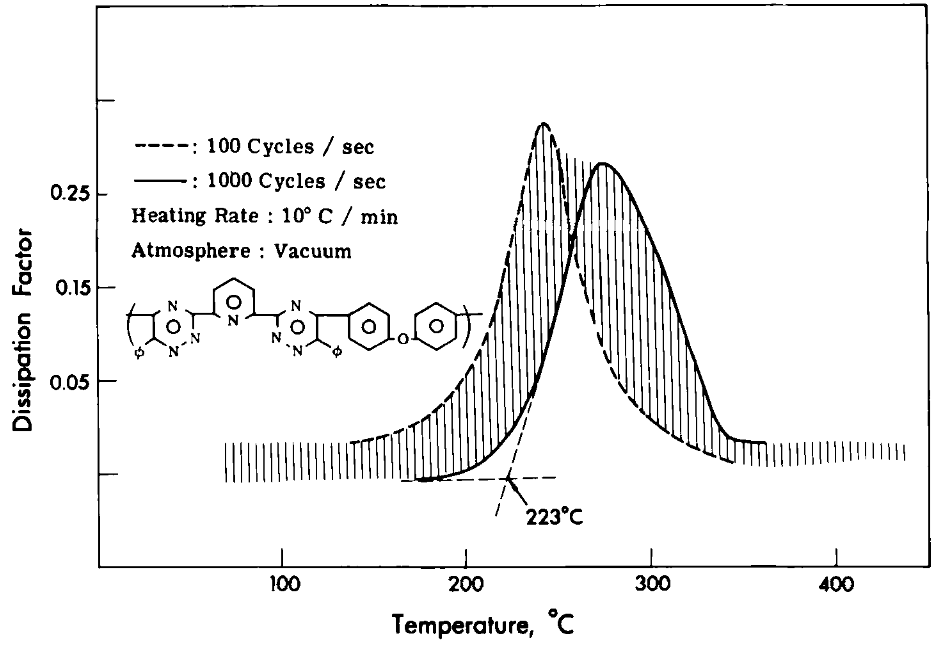


Fig. 1. Dielectric loss spectrum of polyphenyl-as-triazine.

As expected, the polyphenyl-as-triazine containing the rigid p-phenylene moiety exhibited the highest T_g while the polyphenyl-as-triazines containing flexibilizing moieties such as diphenyl ether and diphenyl methane displayed lower T_g's (Table 4).

The thermal stability of the polymers was determined by thermogravimetric (TGA) and isothermogravimetric analyses (ITGA). A typical thermogram for Polymer IP is shown in Fig. 2. As previously indicated [1], as-triazine polymers undergo a two-stage decomposition in both air and nitrogen and exhibit higher apparent stability in air than in nitrogen. The temperature of initial weight loss (T_1) and the temperature of the initial break (T_2) as shown in Table 4 is higher in air than in nitrogen for all polyphenyl-as-triazines except the polymer containing the diphenylmethane moiety (IIIP). An investigation [6] on the thermal degradation of Polymer IVP in vacuo was recently conducted which showed that initial decomposition occurs in the as-triazine ring by thermal cleavage of the N—N bond eliminating benzonitrile to yield a stable intermediate which subsequently degrades. No

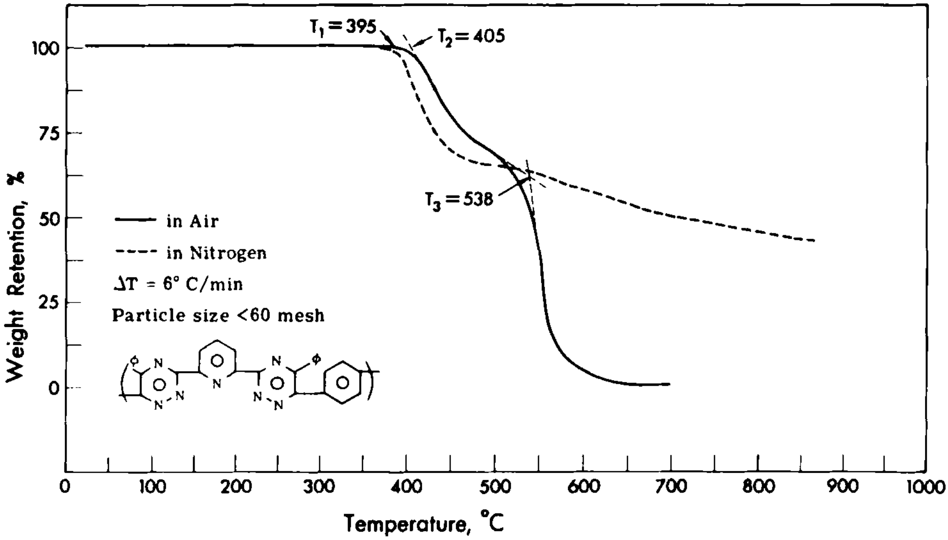


Fig. 2. Thermogravimetric analysis of polyphenyl-as-triazine.

insight was gained, however, to explain why as-triazine polymers exhibit higher apparent stability in air than in an inert atmosphere.

The polyphenyl-as-triazines exhibited excellent stability at 260°C (500°F) in air but at 290°C (554°F) significant weight losses (20-25%) occurred after 45 hr. Isothermal weight loss data is given in Table 4.

Mechanical Properties

Polymer IVP underwent preliminary evaluation in application work as an adhesive and resin matrix in composites. No optimization of process parameters such as surface preparation, primer, filler, or cure conditions was performed. The specimens were fabricated under process conditions derived from preliminary flow tests which were thought to provide specimens suitable for initial testing.

Standard tensile shear specimens were fabricated on abraded titanium (6Al-4V) substrate using an unfilled tape prepared by solution coating 112-A 1100 carrier followed by drying in a forced air oven at 300°F to a volatile content of <5%. The bonds were cured in an autoclave starting at room temperature and increasing the temperature to 550°F during ~30 min and maintaining at 550°F for 1 hr under 35 psi. The resulting

Table 5. Preliminary Mechanical Properties of Polyphenyl-as-triazine Unidirectional Morganite I Laminates

Test	Flexure strength, psi		Modulus, psi X 10^6		Interlaminar shear,[a] psi	
condition	Unpostcured	Postcured	Unpostcured	Postcured	Unpostcured	Postcured
RT	78,000	85,000	30	32	5100	5400
300°F after 10 min	68,000[b]	84,000	26[b]	32	3400[b]	5100
500°F after 10 min	47,000[b]	81,000	16[b]	29	– [b]	4800

[a] Straight beam, span to depth ratio 8:1.

[b] Thermoplastic failure.

tensile shear specimens exhibited average room temperature strength of 2500 psi, and after aging for 2000 hr at 500°F in air, the average room temperature strength was 2100 psi. No testing was performed at elevated temperature and all failures were adhesive type.

Small (2 in. X 4 in. X 9 ply) unidirectional Morganite type I laminates were fabricated at 550°F for 1 hr under 200 psi from prepreg dried at 350°F in vacuo to a total volatile content of <2%. The resulting laminates had void contents of <1% and resin contents of ~28%. As indicated in the test data in Table 5, thermoplastic failure occurred at elevated temperature for unpostcured laminates while laminates postcured in nitrogen through 2 hr at 550°F showed no thermoplastic failure.

CONCLUSIONS

High molecular weight polyphenyl-as-triazines are readily prepared in solutions and exhibit good solubility in a variety of solvents. Films cast from solution exhibit good flexibility and toughness. The phenyl-as-triazine polymers exhibit good stability at 260°C (500°F) in air but undergo substantial weight losses at 290°C (554°F). By TGA, these polymers exhibited polymer decomposition temperatures of ~400°C in both air and nitrogen. Preliminary application work indicated the potential use of polyphenyl-as-triazines as adhesive and laminating resins at temperatures up to 500°F in air.

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