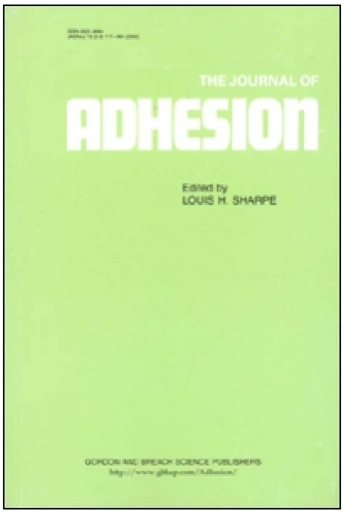

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Toughening of AT-Resins with a Polyphenylquinoxaline[†]

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Acetylene terminated (AT) resins are addition-curable thermoset materials which do not generate volatiles during cure and therefore can be fabricated into void-free structures. They retain good thermal and mechanical properties even after exposure to high humidity environments. Their use as composite matrix resins and adhesives has shown promise. These resins, however, are brittle. Molecular structure modifications and blending with thermoplastic modifiers have been used to improve their toughness. In this work, improvement in toughness has been sought through the use of a polyphenylquinoxaline (PPQ) modifier. The blended systems showed improvements in toughness, thermooxidative stability, and lap shear strength over the original AT-resins.

KEY WORDS Acetylene terminated (AT) resins; toughened AT-resins; AT-resins based on benzophenone and diphenyl sulfone; polyphenylquinoxaline (PPQ) as a toughener; blends of AT-resins with PPQ; adhesive properties of AT-resins.

INTRODUCTION

Over the years, synthetic work on the high temperature resins has generated a number of materials with impressive thermal stability. Many of them however, have been so difficult to process into useful structural forms that the term "brickdust" was employed to describe them. Very high temperatures and pressures were required for the production of void-free structures. Thus, recent synthetic efforts have been directed towards the preparation of more easily processable resins. Addition-curable resins which do not generate volatiles during cure are desirable, since they provide void-free adhesive bonds and composite structures as well. Addition-curable systems such as, maleimide, norbornenyl,

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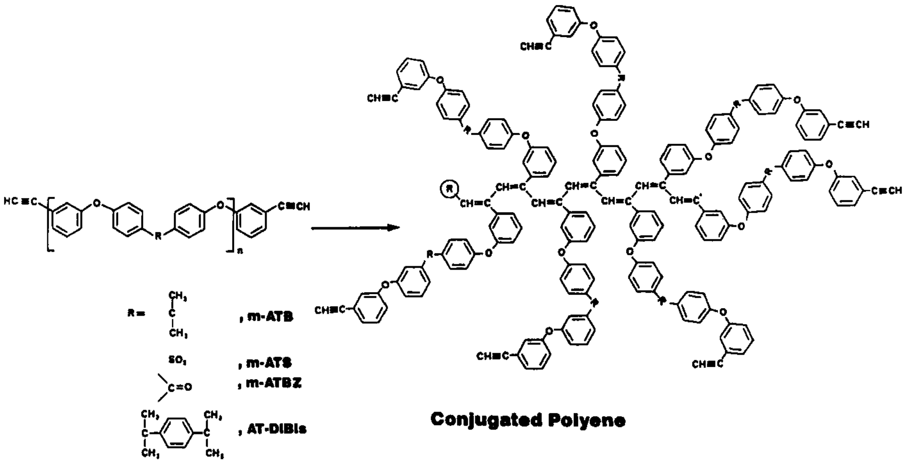


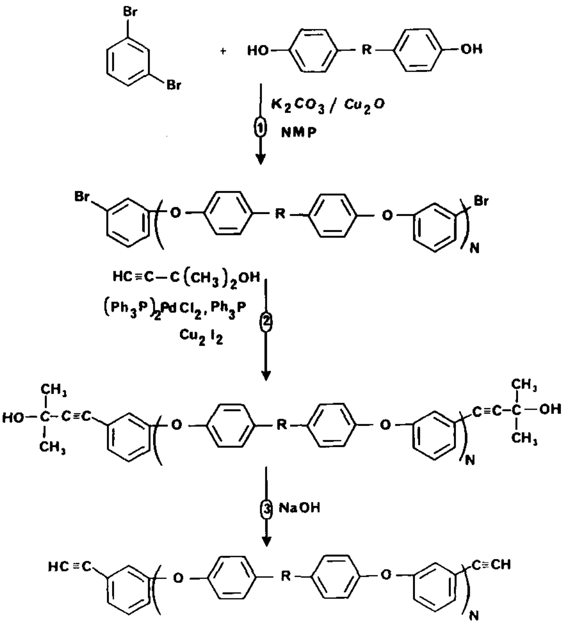
FIGURE 1 Structure of cured AT-resins.

and acetylenic end-capped monomers/oligomers have received much attention. Acetylene terminated (AT) resins, whose chemistry is depicted in Figure 1, show a great potential as structural materials.[1] They are easily processable resins with little loss of thermal properties when exposed to humid environments. The resins, however, are not tough. One approach to imparting toughness has been the addition of thermally stable high molecular weight modifiers.[2] This paper describes some further work to improve toughness using a polyphenylquinoxaline as a modifier. Such improvement was obtained without sacrificing the desirable high temperature properties of the original AT-resins.

EXPERIMENTAL

AT-Resins

The various AT-resins used in this study were synthesized in high overall yield (88+%) *via* a general three-step process described in Figure 2 (based on published procedures developed by the U.S. Air Force Wright Aeronautical Laboratories/MLBC).[3] The first step involved a condensation of a diphenol with excess dibromobenzene to yield a bromophenyl end-capped Ullmann ether product. In the second step, the Ullmann product was reacted with 2-methyl-3-butyn-2-ol in the presence of palladium and copper catalysts to generate an acetone-blocked AT-resin. The third step used a base for deblocking to give the final AT-resins. Residual palladium and copper catalysts, which can adversely affect the thermal stability of the AT-resins, were removed *via* diamine washings. The amount of these catalysts in the AT-resins, determined by energy-dispersive X-Ray fluorescence spectroscopy, was less than 20 ppm. All of the AT-resins used in this study were purified by column chromatography using silica gel as the



N ≥ 1
R = $C(CH_3)_2$, SO_2, C=O etc...

FIGURE 2 Synthesis of AT-resins.

adsorbent and hexane/ethyl acetate (1:1) as eluent. The monomer–oligomer ratio (~4:1) in the resins was determined by GPC and HPLC. All the other characterization data for the AT-resins used in this work have been published earlier.[2]

Polyphenylquinoxaline (PPQ)

The PPQ modifier used in our formulation work was provided by Philip A. Hunt Chemical Corp. as a 10% solids solution in *m*-cresol/xylene. The PPQ was isolated by precipitation in methanol. Its glass transition temperature (T_g), as determined by DSC, was 287°C. The molecular weight for this particular batch of PPQ was not determined, but the high viscosity of the solution and the T_g were completely consistent with the properties of other batches determined to be of high molecular weight. Thermogravimetric analysis showed the isolated material to be solvent-free. The PPQ polymer was prepared in the manner shown in Figure 3.

Preparation of blends

The AT-Resins and PPQ mixtures were dissolved in chloroform and the solvent was evaporated while stirring. The last traces of the solvent were removed under

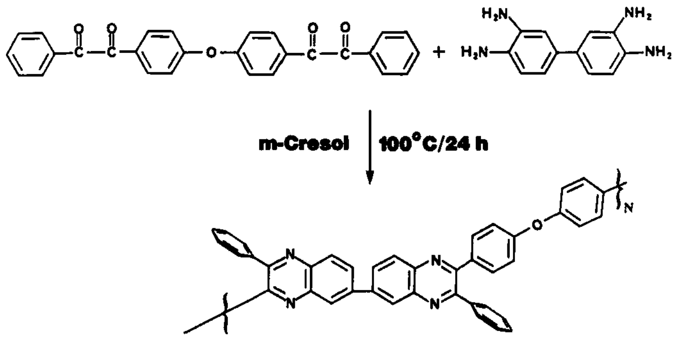


FIGURE 3 Preparation of polyphenylquinoxaline (PPQ).

vacuum. The resulting blends were transferred to molds for preparation of resin plaques which were utilized to fabricate test specimens.

Cure schedule

All of the formulated resins and lap shear panels were cured in a autoclave at 0.41 MPa (60 psi) pressure using the following cure schedule:

22°C to 65°C	5 minutes
65°C	hold for 1 hour 45 minutes
65°C to 100°C	5 minutes
100°C	hold for 45 minutes
100°C to 177°C	5 minutes
177°C	hold for 5 hours
Post Cure (Free Standing)/Air	
278°C	4 hours

Preparation of test specimens

From the above cured plaques, several types of test specimens were prepared.

A. Dynamic Mechanical Thermal Analysis (DMTA) Test Specimens The T_g for the cured materials were determined using a Dynamic Mechanical Thermal Analyzer from Polymer Laboratories Ltd. The DMTA specimen were cut to a dimension of 26–28 × 7.5–10.0 mm and of thickness from 1.25–1.75 mm. The temperature corresponding to the highest point on the tan δ curve was selected as the T_g for the system.

B. Compact Tension Test Specimens (G_{Ic}) The G_{IC} specimens were prepared[4] and the measurements were performed according to ASTM E399-78a. The specimens were machined according to the specifications. While the specimens were being observed under a microscope, a sharp precrack was initiated. The testing was done at room temperature, using an Instron Universal Tester at a crosshead speed of 1.25 mm (0.05 inch)/minute. From the load required to propagate the precrack through the cured resin specimen, the resin modulus from DMTA and Poisson's ratio, the G_{Ic} were calculated.[5]

C. Tensile Lap Shear Specimens Single overlap tensile lap shear specimens were prepared, according to ASTM method D1002, from phosphoric acid-anodized, high temperature-tempered 2024-T81 bare aluminum. The formulated resins were spread over the preheated adherend panels and a 0.025 mm (1 mil) thick glass scrim cloth was laid over the partially-melted resin. The overlap dimensions were 12.5 mm × 25 mm. After the cure, following the above cure schedule, lap shear test specimens were tested on a Model 60 United Mechanical Tester.

RESULTS AND DISCUSSION

Resin bulk properties

The detailed properties of AT-resins included in the present study were reported[2] earlier by Sachdeva and Mahoney. Benzophenone-based AT-resin (ATBZ) was selected for most of the PPQ formulations because of its low viscosity, low moisture absorption, solvency, and high temperature properties. Two additional AT-resins, 4,4′-bis(3-ethynylphenoxy)diphenylsulfone (*m*-ATS) and 2,2′-[4-(3-ethynylphenoxy)phenyl]propane (*m*-ATB), were also included as potential candidates for the toughening studies. The high-temperature properties of the *m*-ATS resin appeared attractive[6] for blending studies. However, some compatibility and processing problems were experienced during mixing with PPQ. Further investigations with the *m*-ATS were not attempted. The fracture toughness (G_{Ic}) of the AT-resins is given in Table I. As can be seen, the AT-resins are not at all tough materials. A somewhat higher G_{Ic} for the AT-resin derived from α,α'-bis(p-hydroxyphenyl)-p-diisopropylbenzene (AT-DiBis) is offset by its low thermooxidative stability as determined[2] by TGA. The SEM picture (Figure 4) of the fracture surface of the ATBZ resin showed a grading pattern which is typical of brittle resins. The other AT-resins showed the same brittle surfaces in similar studies. The need to toughen these resins to provide useful properties is evident.

TABLE I
Fracture toughness of AT-resins

AT-Resins	$G^{\ddagger}_{Ic}$(in-lb/in^2)	[J/m^2]
m-ATB	<0.2	[<3.56]
m-ATS	<0.02	[<3.56]
p-ATS*	<0.02	[<3.56]
m-ATBZ	0.02	[3.56]
m-AT-DiBis	0.4	[71.2]

* For this AT-resin, the acetylene group is located at the para position in Figure 1.

‡ Measured by compact tension method.

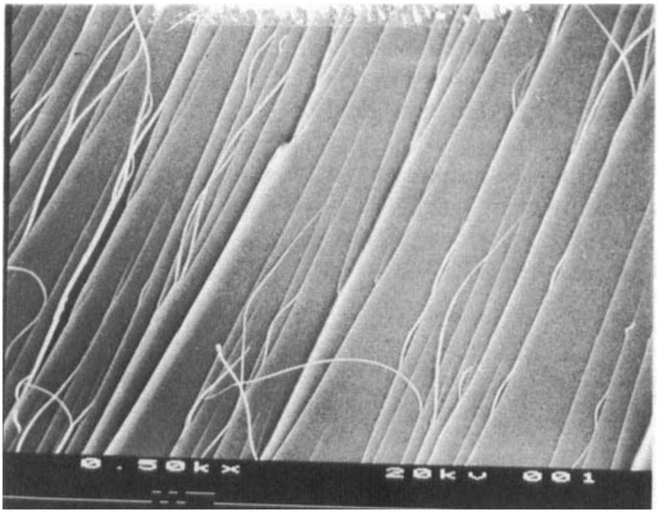


FIGURE 4 SEM photograph (500 × magnification) of the cured ATBZ resin fracture surface.

BLENDING STUDIES

Flow properties of blends

The blends of the AT-resins with PPQ were dark-colored, thick oils. The resin flow properties of ATBZ and its blend containing 5% and 10% PPQ were measured using a Rheometric Viscoelastic Tester. There was a steady increase in viscosity with the increasing amounts of PPQ used (Figure 5). The 10%

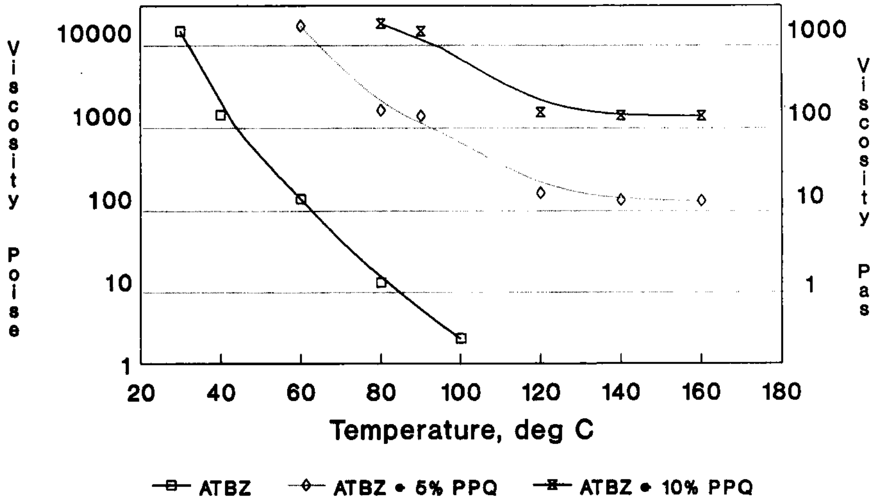


FIGURE 5 Viscosities (parallel plate method) of PPQ blended systems and neat ATBZ resins.

PPQ + ATBZ blend, a thick oil, showed viscosity of ~100 Pa.s (~1000 poise) at 137°C and was still processable.

Thermal properties (T_g and thermooxidative stability)

In the past, improvement in the toughness of thermoset resins through addition of engineering thermoplastics or rubbers have been compromised by some loss of other desirable properties. The addition of tougheners often reduces the crosslink density in the thermoset materials and the T_g is lowered. The addition of PPQ to the thermally-crosslinkable AT-resins, however, did not reduce the T_g. Cured blends containing ATBZ and PPQ had T_g either equal to or slightly higher than that of the cured neat ATBZ (Table II). The T_g for some additional cured blends from *m*-ATB, *m*-ATS, and AT-DiBis and containing varying amounts of PPQ were still high (Table III). No secondary peak due to a second toughener phase was observed in the tan δ curve of the DMTA runs (this is usually observed in toughened thermoset systems). A multiple blend also containing AT-DiBis [a material with lower T_g (260°C, Figure 6) and higher toughness than ATBZ and m-ATB], with PPQ resulted in a system with higher T_g (304°C, Figure 7 and Table III) than the parent AT-resins. This unusual effect is not fully understood, but similar observations have been reported by Kinloch[7] and St. Clair[8] in the rubber modification of polyimides.

The addition of PPQ did not decrease the thermooxidative stability of the

TABLE II
Glass transition temperature of ATBZ formulations

Resin	T_g*	(°C/F)
ATBZ	290	554
ATBZ + 5% PPQ	303	577
ATBZ + 10% PPQ	297	566

* Determined by Dynamic Mechanical Thermal Analyzer at a heating rate of 4 degree C/min.

TABLE III
T_g for AT-Resins & their formulations

AT-Resin/Formulation	T_g*	(°C/F)
m-ATS	360	680
m-ATS + 5% PPQ	389	732
m-ATS + 10% PPQ	385	725
m-ATB	275	527
AT-DiBis	260	500
ATBZ + PPQ + AT − DiBis + ATB (7:1:1.5:0.5)	304	579

* Determined by Dynamic Mechanical Thermal Analyzer at a heating rate of 4 deg. C/min.

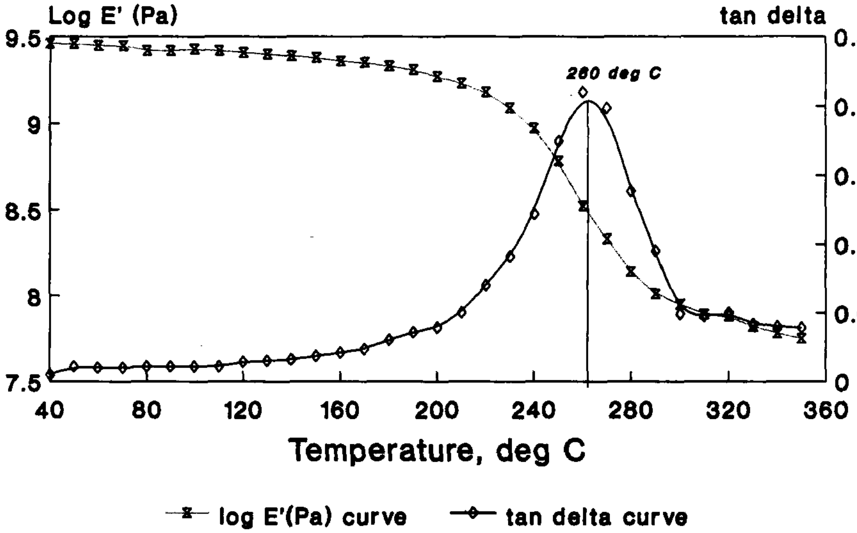


FIGURE 6 T_g (DMTA method at a heating of 4 deg C/min) for AT-DiBis Resin: Modulus *vs* tan δ.

AT-resins (Figures 8–10). During the thermogravimetric (TGA) tests in air, using cured powdered samples to maximize the surface exposure, blends of PPQ with ATBZ and *m*-ATS (Figures 8 and 9) showed lower weight loss rates than did the precursor AT-resins. The other PPQ blends also showed improved thermal stability (Figure 10) in air over the AT-resins alone.

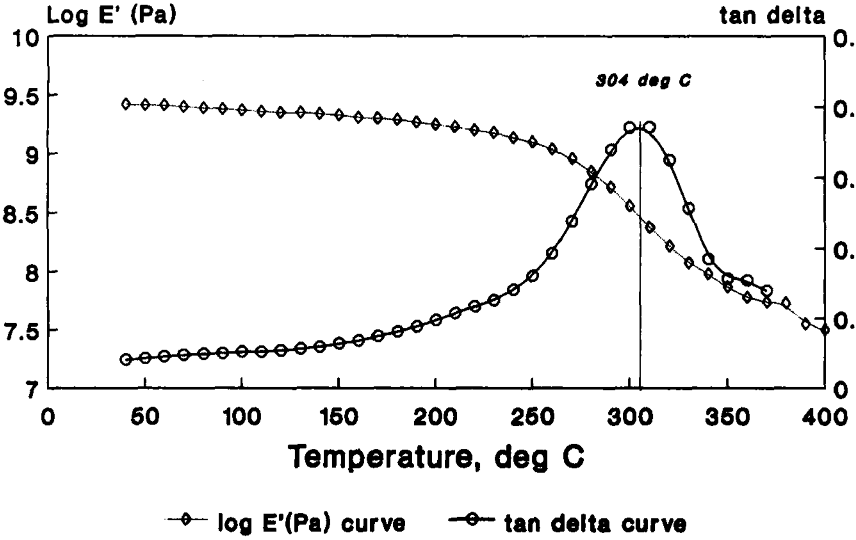


FIGURE 7 T_g (DMTA method at a heating rate of 4 deg C/min) for AT-DiBis formulations: Modulus *vs* tan δ.

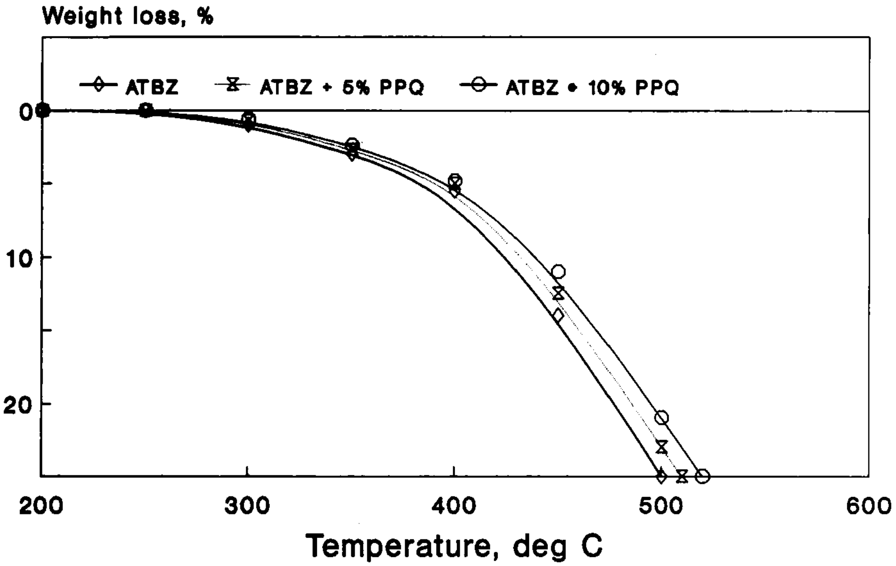


FIGURE 8 Thermooxidative resistance (TGA method at a heating rate 5 deg C/min in air) of ATBZ & PPQ blends.

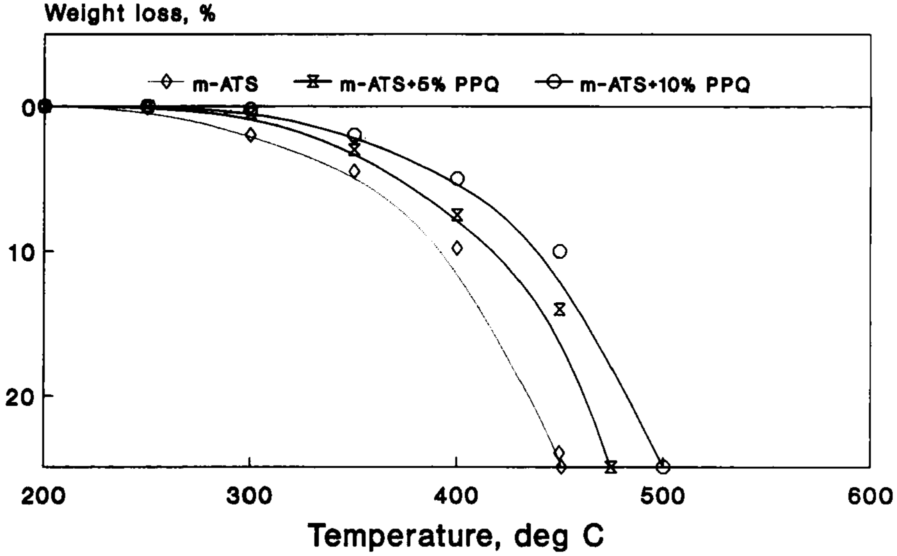


FIGURE 9 Thermooxidative resistance (TGA method at a heating rate of 5 deg C/min in air) of ATS & PPQ blends.

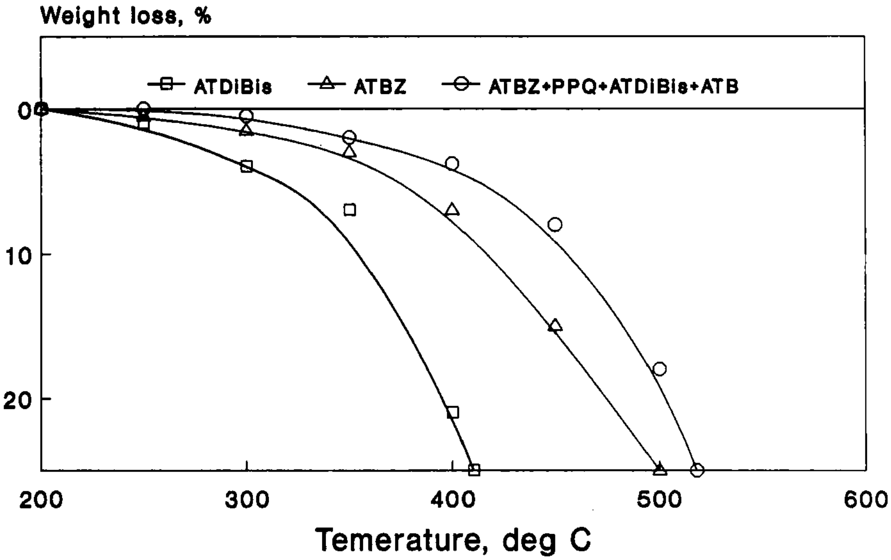


FIGURE 10 Thermooxidative resistance (TGA method at a heating rate of 5 deg C/min in air) of AT-resins & PPQ blends.

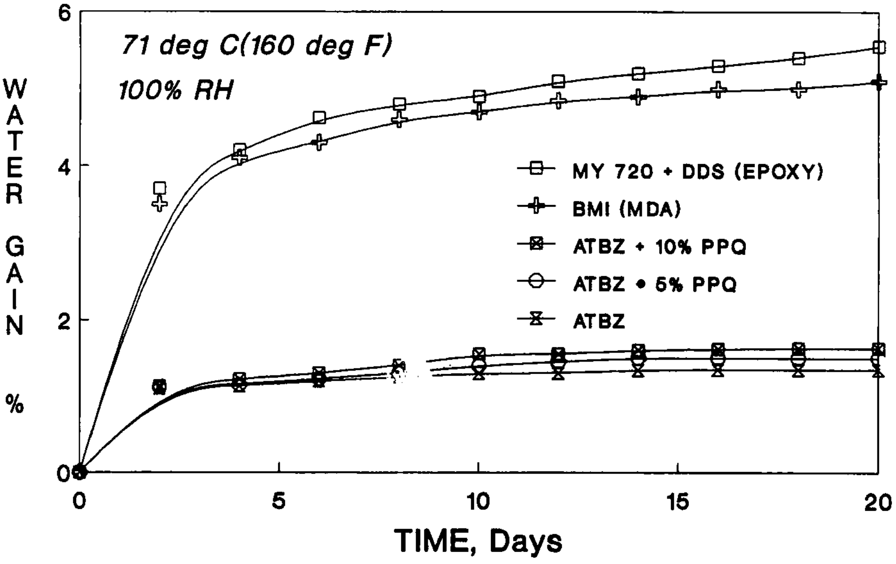


FIGURE 11 Comparison of water absorption level for formulated ATBZ & other resins.

Moisture equilibration

The moisture absorption for PPQ blends was very close to that of the neat ATBZ resin. As shown in Figure 11, exposure at 71°C (160°F) and 100% RH over a period of 20 days, resulted in <2% water absorption by the formulated resins. The levels of moisture absorption for other high temperature thermoset resins, such as epoxy (MY 720 + DDS) and BMI (MDA) systems, were two to three times higher than for the ATBZ blends.

Fracture toughness

The effect of PPQ addition on the fracture toughness of the ATBZ was encouraging. The G_{Ic} values were found to increase with increasing amount of PPQ in the blends (Table IV). A *tenfold* increase in the fracture toughness was observed with ATBZ blend containing 10% PPQ. The SEM pictures (Figure 12) of the fracture region of the ATBZ and PPQ blends showed a tougher failure pattern.

Adhesive properties

Formulations of PPQ with ATBZ showed a significant increase in the tensile lap shear strength over a wide temperature range (Figure 13). The tensile lap shear values for 10% PPQ-ATBZ exceeded 11 MPa (1.5 KSI) from ambient temperature to 315°C (600°F) which was about 5 MPa (0.4–0.5 KSI) higher than the resin alone. The failure mode for the ATBZ and PPQ blends was less brittle than with the neat resin (Figure 12). Some bond failure at or close to the metal surface, and from the glass scrim cltoh, is partly responsible for the data fluctuation (±10%). It suggests directions to take in improving the bond strengths in future work. PPQ-containing blends from *m*-ATS and AT-DiBis showed little or no improvement in the tensile lap shear values (Figures 14 and 15) over the AT-resins alone.

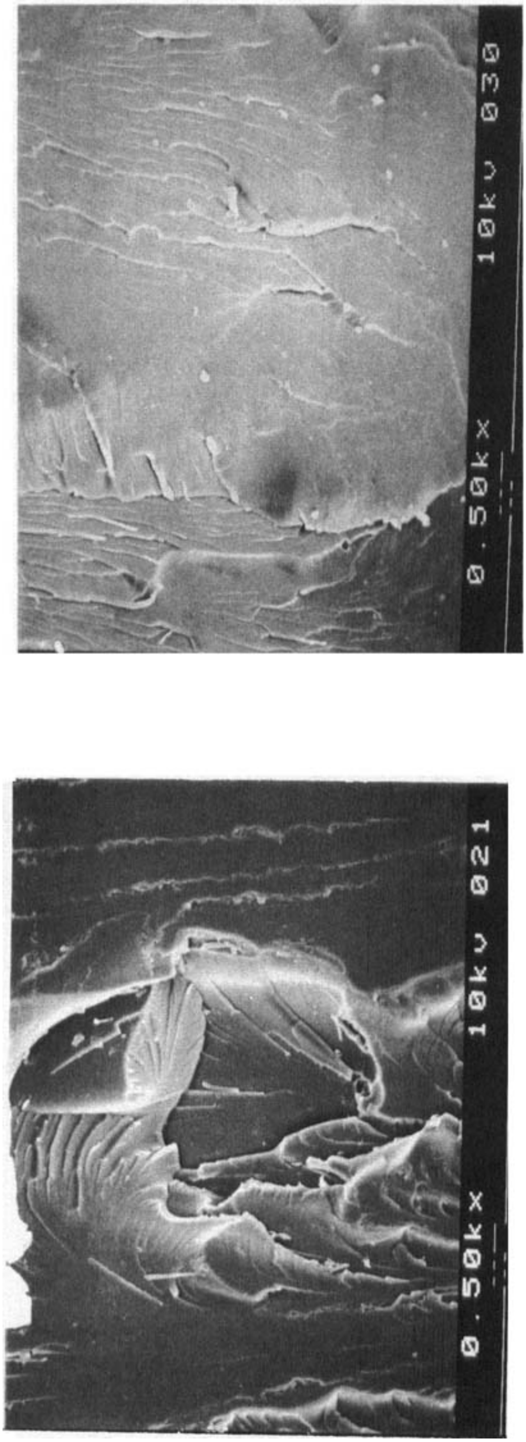
SUMMARY & CONCLUSION

Benzophenone-based AT-resin (ATBZ) forms compatible blends with PPQ. Blends of PPQ with ATBZ have enhanced some of the desirable properties

TABLE IV
Fracture toughness (G_{IC})* measured of ATBZ formulations

Resin	G_{Ic} in-lb/in^2	J/m^2]
ATBZ	0.02	[3.6]
ATBZ + 5% PPQ	0.18	[32]
ATBZ + 10% PPQ	0.22	[39]

* Measured by compact tension method.



a: ATBZ + 5% PPQ

b: ATBZ + 10% PPQ

FIGURE 12 SEM photographs (500 × magnification) of the fracture surface of PPQ modified-ATBZ resins

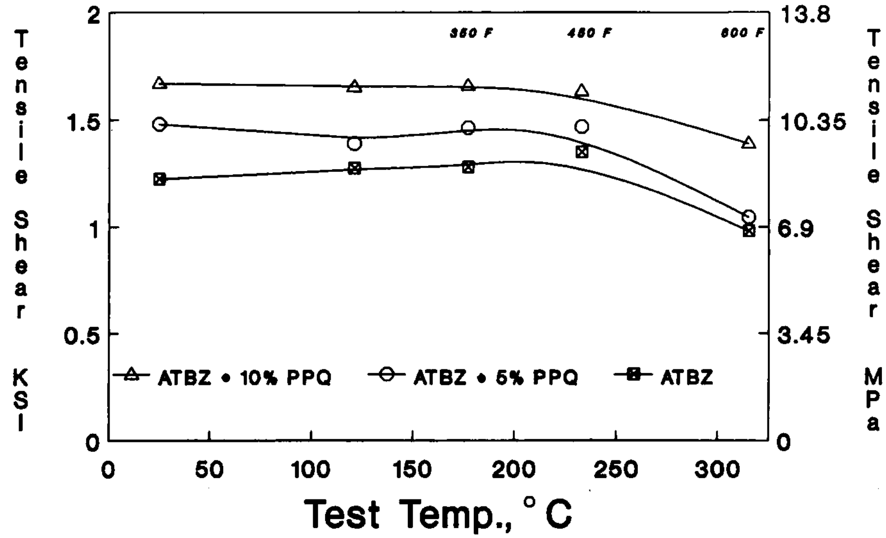


FIGURE 13 Tensile lap shear strength (2024-T81, PA aluminum) of ATBZ and its modifications.

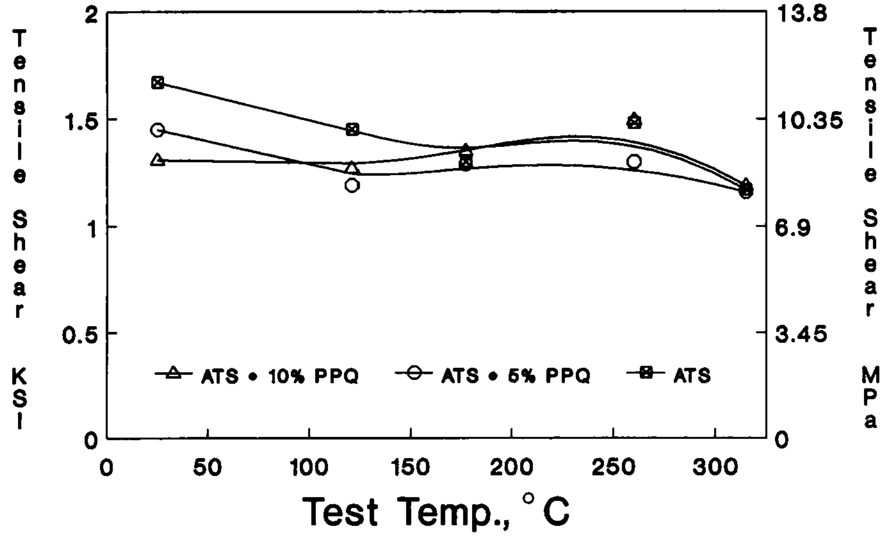


FIGURE 14 Tensile lap shear strength (2024-T81, PA aluminum) of ATS and its modifications.

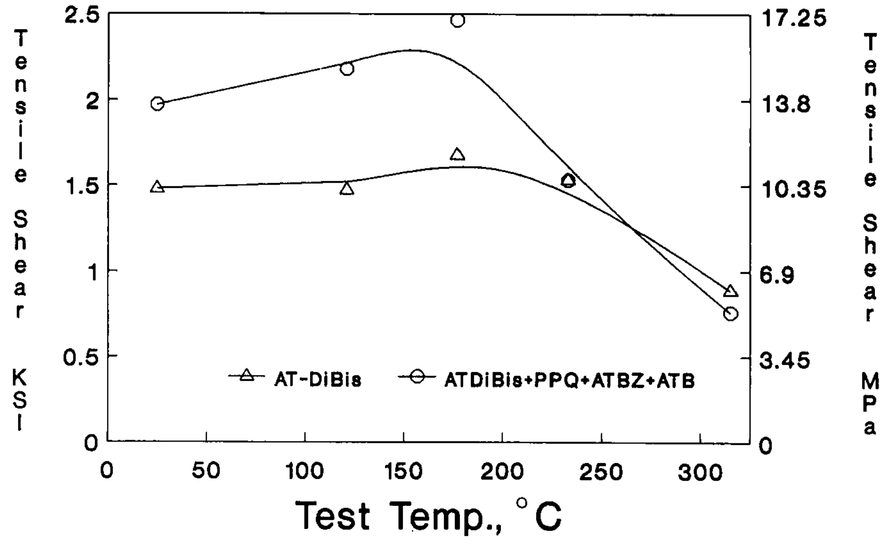


FIGURE 15 Tensile lap shear strength (2024-T81, PA aluminum) of AT-DiBis & its modicfiations.

without degrading others. The formulated systems are tougher than the resin alone. The addition of PPQ neither increases the water absorption nor affects the viscosities significantly. Inclusion of PPQ in the systems also increases the thermooxidative stability.

Acknowledgement

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