RTM MOLDING STUDY OF CITRACONIC ANHYDRIDE END CAPPED POLYIMIDES

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Keywords: Polyimide, RTM Molding, High Temperature Resin

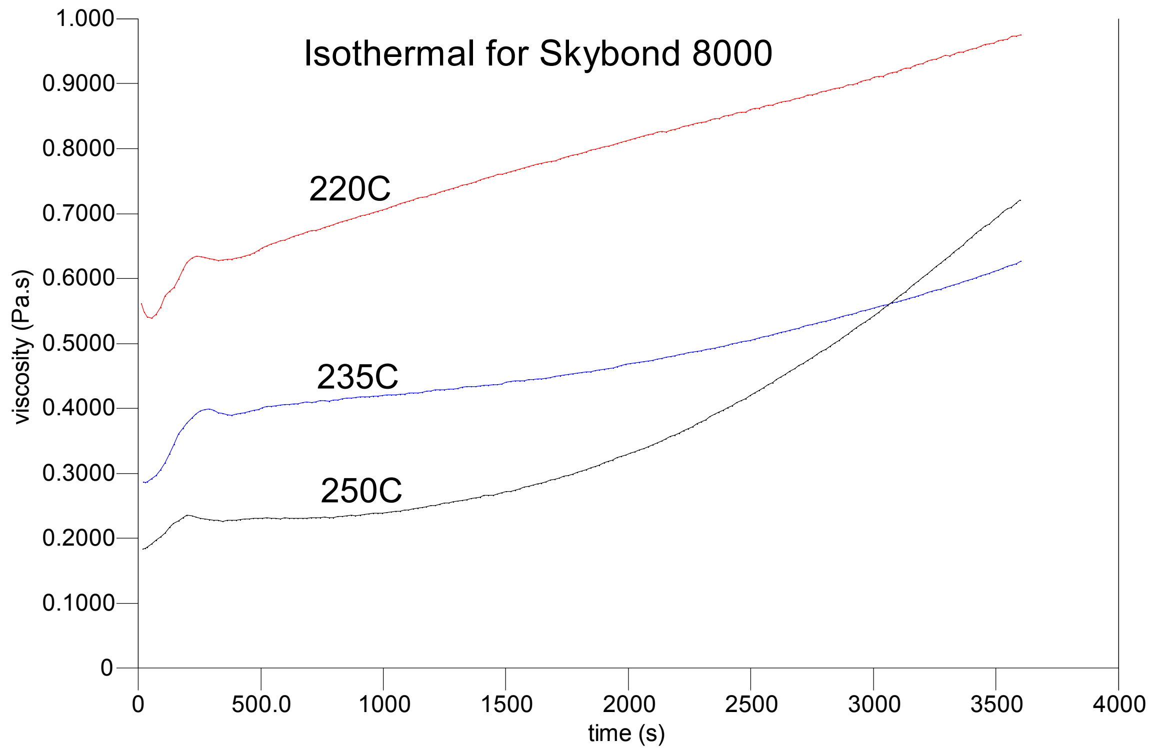
1.0 Abstract

A strong drive has developed to reduce manufacturing costs of high temperature composites. The main emphasis of this effort has been to replace condensation cure polyimides by systems with addition cure end caps to control volatiles during cure. These efforts have led to definition of resin systems with good performance, but the cost of the resins is high due to cost of the end cap and monomers. This paper describes a study of RTM molding conditions for polyimides with citraconic anhydride end caps. This resin system has acceptable viscosity for molding (Figure 1) and a good balance of properties (Table 1) with significant reduction in cost compared to other RTM capable polyimide systems. The resins discussed in this paper bring a family of affordable polyimides capable of being molded by an RTM process to the high temperature composite industry.

Table 1
High Temperature Flexural Strength
Molded at 235º C; Cured 350º C for 60 minutes

Temperature	Skybond® 6000	Skybond® 8000
Room Temperature	670 Mpa	690 Mpa
177º C	1000 Mpa	1050 Mpa
204º C	870 Mpa	Not Measured
232º C	Not Measured	910 Mpa
246º C	Not Measured	630 Mpa

Figure 1



2. INTRODUCTION

Polyimides have been the main resins employed in the manufacture of high temperature structural composites for over 40 years. Early condensation polyimides, such as, Skybond developed by Monsanto (now sold by Industrial Summit Technology) and Avimid developed by DuPont have had their utility limited by the very complex cure schedules necessary to obtain composites with acceptable porosity. It has long been recognized that the cure volatiles generated in the condensation cure resins are responsible for porosity in the composite and the complex cure schedules.

The first attempt to solve the cure volatile issue was development of nadic anhydride end capped resins by NASA Lewis and TRW (1). The concept behind this innovation is to control molecular weight of the polyimide with an end cap that will allow cure volatiles to be removed. After removal of cure volatiles the resin will possess sufficient flow that voids can be removed by applying pressure and finally curing the resin through the end caps via a non-volatile producing addition cure mechanism.

The resins based on nadic anhydride while enjoying some success in commercial use were not universally accepted due to the use of methylenedianilne in the product and generation of volatiles during cure from decomposition of nadic anhydride to form cyclopentadiene. In the early 1990's NASA developed a family of polyimides based on phenylethynylphthalic anhydride (PEPA) end caps (2). The resins based on PEPA end caps had good two-stage cure performance and have been shown to be capable of RTM processing (3). The issue with the PEPA based systems is the cost of the resins. The raw materials used in the PEPA based systems are available only in small quantities and are therefore quite expensive. Thus although, manufacturing cost reductions can be realized with these systems overall cost reduction is limited due to high cost of resins.

This report will describe a molding study of a family of developmental polyimide resins based on relatively low cost raw materials. The resins described in this paper are capable of being processed by either RTM molding or 'two-stage' cure prepreg operations. This family of resins will allow the reduced processing costs of RTM and 'two-stage' cure systems to be realized with resins having traditional polyimide cost structure.

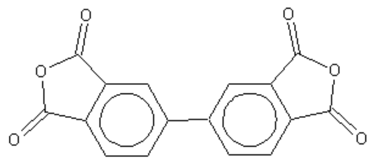
3. EXPERIMENTAL PROGRAM

3.1 Raw Material Selection

The basis for the synthesis program was to utilize commercially available diamines and dianhydrides that are priced below $50 per pound and are on the TSCA inventory. The reason for this restriction was to ultimately have a maximum price for the new polyimide of $100 per pound. TSCA listing of the raw materials is important to be able to obtain PMN approval of the new polyimides and be able to manufacture without volume restrictions. The most challenging issue was identification of an end cap meeting these criteria other than maleic anhydride or nadic anhydride that both have performance limitations.

Beyond cost and TSCA listing, the monomers chosen must produce oligomers that have melt viscosities low enough to allow RTM molding. The reactive end cap must have good stability to allow an adequate processing window before viscosity increases to point where molding is not possible. A melt viscosity below 1.0 PaS for a period of one hour at the processing temperature should give an adequate window for molding and was criteria used to judge moldability. After molding the end cap should cure at a temperature obtainable in conventional high temperature presses to allow part curing. We considered a cure temperature of 375º C to be the maximum temperature allowable for cure. The monomers and end cap listed in Figure 1 were found to allow synthesis of oligomers that met these criteria.

Figure 1



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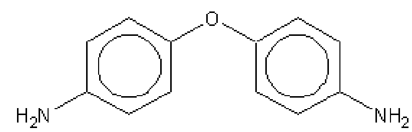
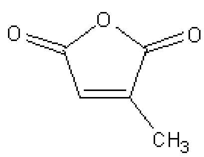


44'-ODA



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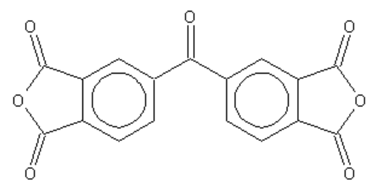

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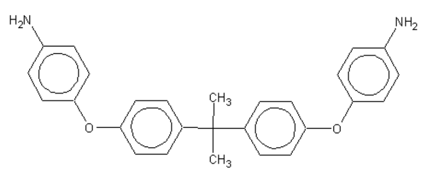

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3.2 Synthesis Method

A solution of dianhydride is added over a two hour to a solution of diamine in n-methylpyrrolidone. After the addition of the dianhydride the end cap is added over a period of one hour. Toluene and a ring closure catalyst is than added and water is removed via azetropic distillation. After water removal is complete toluene is removed by vacuum distillation at pressure of 25 milibars and 120º C. The product is isolated by pouring solution into water (10:1), filtering and drying in air oven.

3.3 Viscosity Measurement

Material/Equipment:

1. TA Instruments Advanced Rheometer AR 1000 with computer and instrument software
2. Geometry (Sample plates, Disposable or Permanent, diameter 25 and 40mm)
3. Carver pellet maker 4350
4. Samples (varnish or powder)
5. Wrenches
6. Agate mortar
7. Vacuum oven
8. Aluminum pan
9. Balance

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Sample Preparation**:**

In general, powder sample need to be degassed before running viscosity measurement. Weigh around 1.5 ~ 2 grams powder in an aluminum pan and then degas the sample in a vacuum oven at 30 in Hg and 220 °C for 20 minutes. Grind the degassed sample with an agate mortar and weigh about 1 gram of the ground sample to make a pellet using the Carver pellet maker with a 2.5-cm diameter die.

Parameters for Temperature Scan Viscosity**:**

1. Oscillation: 100 radian/sec.
2. Shear Stress: 0.1 Pa
3. Force: 45-50 Newton
4. Temperature Increase: 10º C per minute

Parameters for Isothermal Viscosity:

1. Oscillation: 100 radian/sec.
2. Shear Stress: 0.1 Pa
3. Gap: 500 microns

3.4 Tg Measurement

1. Shimadzu Differential Scanning Calorimeter (DSC-60)
2. Aluminum (Al) cell
3. Temperature Program: Heat 10°C/min to 450°C and hold for 5min, Cool 10°C/min to 150°C and hold for 0min, Heat again 10°C/min to 450°C and hold for 5min.

3.5 Molding Conditions

1. Radius Engineering 2100 cc High Temperature Injector
2. Injection Pressure: 150 psi
3. Injection Rate: 10 cc per minute
4. Injection Temperature: Varied
5. Mold Temperature: 250º C
6. Cure Time and Temperature: Varied
7. Desized T650-35 12K 8HS carbon fabric
8. Flexural Properties: ASTM D-790 (2003)

3. DISCUSSION

After scouting a large number of compositions (4) two compositions were chosen for molding studies. The main criteria for the choice of the compositions for further study were monomer cost and availability, cured resin glass transition temperature and viscosity behavior of the resin. The compositions chosen for molding studies were Skybond® 6000 and Skybond® 8000. The glass transition temperatures for the pure resin cured at 335ºC for four hours are given in Table 1.

Table 1

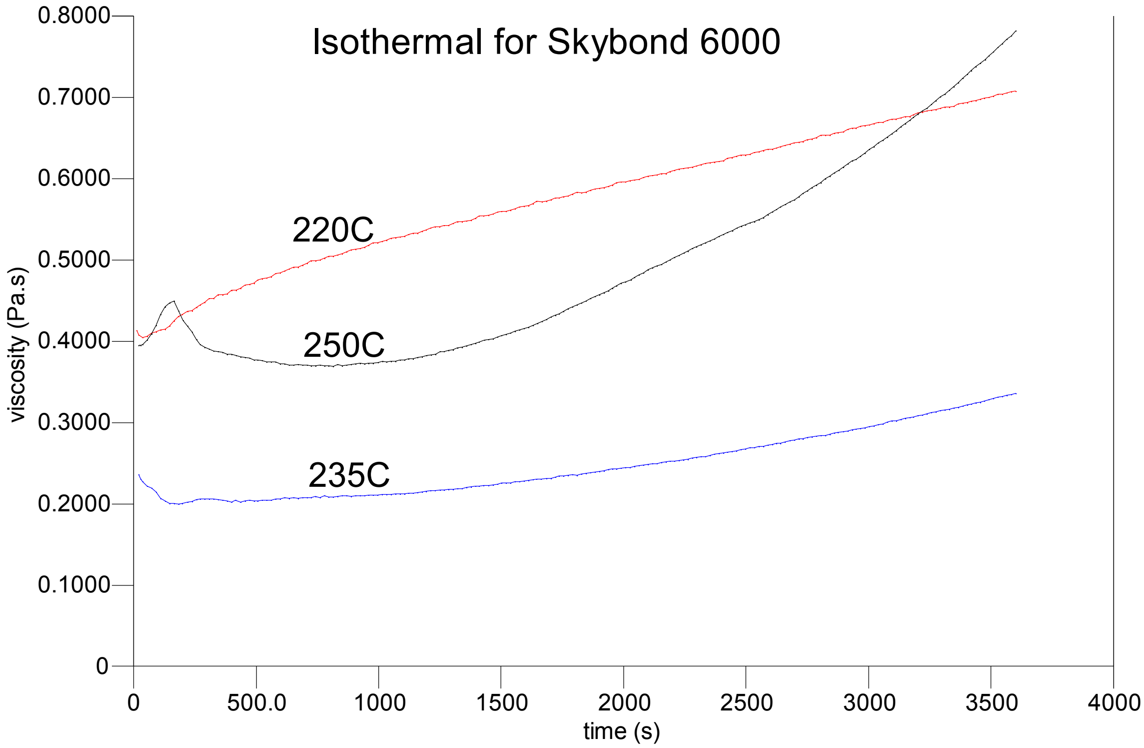
Product	Glass Temperature º C
Skybond® 6000	250
Skybond® 7000	270
Skybond® 8000	295

The viscosities of the compositions chosen for additional evaluations are low enough to allow molding by RTM techniques Figure 1 and 2 and have adequate viscosity stability to allow molding. Skybond 8000 was molded by GKN using T650-35 12K 8HS carbon with sizing. This panel was used to measure short beam shear properties to establish that resin had adequate properties to justify further study. Table 2 summarizes SBS data for Skybond® 8000 compared to published data for PETI-330. One of the criteria for the project was to have resin properties essentially equal to PETI-330 at room temperature and elevated temperature below the glass transition temperature of the Skybond® resin. The comparison of SBS data shown in table 2 indicates that the new resin has shear properties similar to PETI-330 and this information coupled with the viscosity behavior and cost structure of the resin was sufficient justification to continue the study of the effect of molding conditions on panels fabricated with the family of resins.

Table 2
Short Beam Shear

	SK-8000	PETI-330
SBS RT	54 Mpa	56 Mpa
SBS 450º F	40 Mpa	42 Mpa

Figure 1



The molding conditions studied that will be reported in this paper were injection temperature and curing conditions. The basis for RTM processing as explained earlier is a low molecular weight oligomer that is cured through a reactive end cap after molding, therefore curing conditions are critical to performance of the resin. The effect of curing conditions on glass transition temperature is shown in Table 3. The glass temperature is dependent on cure time and temperature varying over about a 10º C range from 265 to 275º C with cure conditions of one hour at 250º C to four hours at 235 º C. This is not unexpected as with this type of resin the glass temperature is very dependent on degree of cross linking and more thermal exposure will increase crosslink density and thus glass temperature.

Figure 2

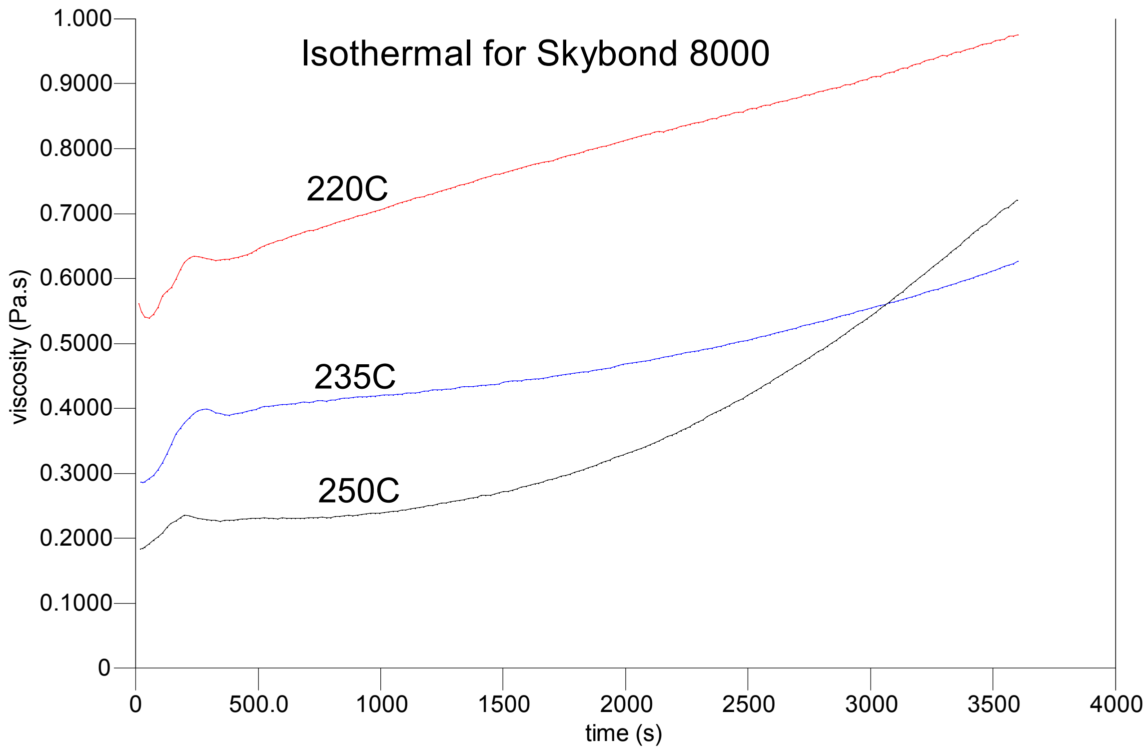


Table 3
Tg versus Cure Conditions

Resin	Cure Temperature	Cure Time	Tg
Skybond® 6000	350º C	60 minutes	235º C
Skybond® 6000	350º C	120 minutes	237º C
Skybond® 8000	350º C	60 minutes	266º C
Skybond® 8000	350º C	120 minutes	270º C
Skybond® 8000	335º C	240 minutes	273º C

The effect of molding temperature and cure conditions on flexural properties is shown in Table 4. Flexural strength and modulus appear to be relatively constant over the range of conditions studied. The main impact of molding temperature and cure conditions appears to be on the glass temperature as shown in Table 3. High temperature flexural properties are shown in Table 5. The high temperature properties are very good for this resin system with good property retention to within 20º C of the glass temperature of the composite.

Table 4
Flexural Strength versus Molding Conditions

Resin Skybond®	Injection Temperature	Cure Temperature	Cure Time Minutes	Tg	Flexural Strength Mpa	Flexural Modulus Mpa
6000	235º C	350º C	60	235º C	690	40000
6000	235º C	350º C	120	235º C	650	39000
8000	250º C	350º C	60	266º C	690	39000
8000	235º C	350º C	60	264º C	700	39000
8000	235º C	350º C	120	270º C	690	40000
8000	235º C	335º C	240	273º C	670	38000

Table 5
High Temperature Flexural Strength
Molded at 235º C; Cured 350º C for 60 minutes

Temperature	Skybond® 6000	Skybond® 8000
Room Temperature	670 Mpa	690 Mpa
177º C	1000 Mpa	1050 Mpa
204º C	870 Mpa	Not Measured
232º C	Not Measured	910 Mpa
246º C	Not Measured	630 Mpa

4. SUMMARY

Polyimide systems that are capable of being molded via an RTM process have been defined based on citraconic anhydride end caps. These resin systems show good latitude in process conditions. The molded panels have good flexural properties and good retention of properties at elevated temperatures with use temperatures up to 250 º C for the higher temperature system. The cost of these systems is very attractive for polyimide systems with a cost below $100 per pound at commercial scale quantities. Future work on other properties, such as, compression properties and thermal aging must be completed to fully define utility of the resins.

5. REFERENCES

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