

STUDY ON ONE PHTHALONITRILE RESIN SYSTEM SUITABLE FOR RTM PROCESS

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Abstract

One phthalonitrile resin system previously developed in our lab had melting temperature around 160°C, which was reported in SAMPE 2011 conference. After modification with one reactive diluent, the resin system could maintain low viscosity at 140 °C for a long time, which was suitable for RTM process. The ratio of diluent in resin system was changed and the influence on processability was studied by Rotational Viscometer. In addition, DSC and TGA were used to research the cure reaction and thermal properties for resin system with different ratio of diluent, respectively. The glass transition temperature was tested by DMA technique. Preliminary study on mechanical properties of carbon/glass hybrid fabric reinforced composite fabricated by RTM was carried out at room and elevated temperature.

1 Introduction

Composite materials, owing to the lightweight and excellent properties, provide a winning combination that propels composites into use as replacements for conventional materials in high-temperature applications. Advanced aerospace vehicles such as high speed aircraft and missiles require high performance/high temperature resins for use as adhesives and composite matrix resins for structural or functional applications. In recent decades, resin transfer molding (RTM) has proved to be a cost effective process for manufacturing composite structures, when compared with prepreg/autoclave techniques. RTM requires a resin with low and stable melt viscosity at injection or infiltration temperature at least ≥ 2 hours. Mostly, high-temperature composites by RTM were investigated and examined for use based on bismaleimides(BMI) and polyimides (PI) as matrix resins[1-2].

Phthalonitrile resins were developed at the Naval Research Laboratory (NRL) in response to the need for processable, high temperature resistant matrix resins for fiber reinforced composites [3-4], which have been studied for the last 30 years and regarded as a class of high temperature polymers. The advantages and versatility of the phthalonitrile polymer, having potential to be used in composite matrices, adhesives, films and electrical conductors, may be realized in terms of processability and striking properties (for instance, when cured, outstanding thermal-oxidative stability, excellent mechanical properties, low water absorption

and superior flame resistance, etc) [5-11]. In addition, the reaction of phthalonitrile monomer with curing additives [3, 6, 12-13] is not accompanied by evolution of volatile byproduct; therefore, void-free components can be fabricated easily. Furthermore, the cure exotherm is low, which should allow thick section composite fabrication. Up to now, prepreg/autoclave and resin infusion process were examined for phthalonitrile composite fabrication [7-8]. However, RTM process was nearly none to be used to fabricate phthalonitrile laminates.

In the past, phthalonitrile monomers with aromatic ether [4, 14-15], imide [16], hexafluoropropylidene [17], sulfone [18-19], bisphenol A [20] and aromatic ether phosphine oxide [5] linkages incorporated between the terminal phthalonitrile units have been synthesized. High temperature of melting transition (usually $\geq 200^{\circ}\text{C}$) is a common shortcoming for these monomers [4, 14-20]. With cure additives such as diamine, the melt viscosity of monomer/additive mixture is low ($< 1\text{Pa}\cdot\text{s}$) after the resin system is melted, however, polymerization begins immediately and results in a short processing window. Short processing window means that the viscosity cannot maintain at this level for a long time (≥ 2 hours for RTM as mentioned above) although the melt viscosity is suitable. The development of the low-melting phthalonitrile monomers emanated from the need for high-temperature phthalonitrile resins with a longer processing window for composite fabrication by non-autoclavable processes such as RTM. The technical challenge is to improve the processability of the phthalonitriles without significantly sacrificing their other desirable properties.

In the previous work a phthalonitrile resin (named SPCN1010) with melting temperature around 160°C was developed and reported in SAMPE 2011 conference and exhibition, which had outstanding mechanical properties at high temperature, maintaining around 50% to room temperature properties at 450°C and 500°C [21]. Rheological study showed the viscosity of SPCN1010 remained below $1\text{Pa}\cdot\text{s}$ for about 90 minutes and 40 minutes at 155°C and 170°C , respectively. This short processing window was not sufficient for RTM methods.

In this paper, one low-melting RTM-phthalonitrile resin was developed on the modification of SPCN1010. The processability was evaluated by rotational viscometer in isothermal conditions. The resin was polymerized at moderate temperatures using self-catalyst agent 4-(4-aminophenoxy)phthalonitrile [22] and reactive diluent. Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) were used to investigate the cure behavior and thermal property of the modified resins compared with SPCN1010. This paper also concerned phthalonitrile/RTM production of 2.5D fabric composite panels and preliminary data on room and high-temperature mechanical properties.

2 Materials and testing methods

2.1 Starting materials

4-nitrophthalonitrile was purchased from Alpha (Shijiazhuang, China) chemical Co., Ltd, and used after recrystallized from ethanol. P-aminophenol were commercially available from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received. Resorcinol, acetone, potassium carbonate, N, N-dimethylformamide (DMF) and sodium hydroxide were used as received from Beijing Beihua Fine Chemicals Co., China. MT300-3K carbon fiber fabric was commercial from Institute of Coal Chemistry, Chinese Academy of Sciences. SW280 glass fabric was purchased from Nanjing Fiberglass R&D Institute.

2.2 Synthesis of monomers and phthalonitrile resin

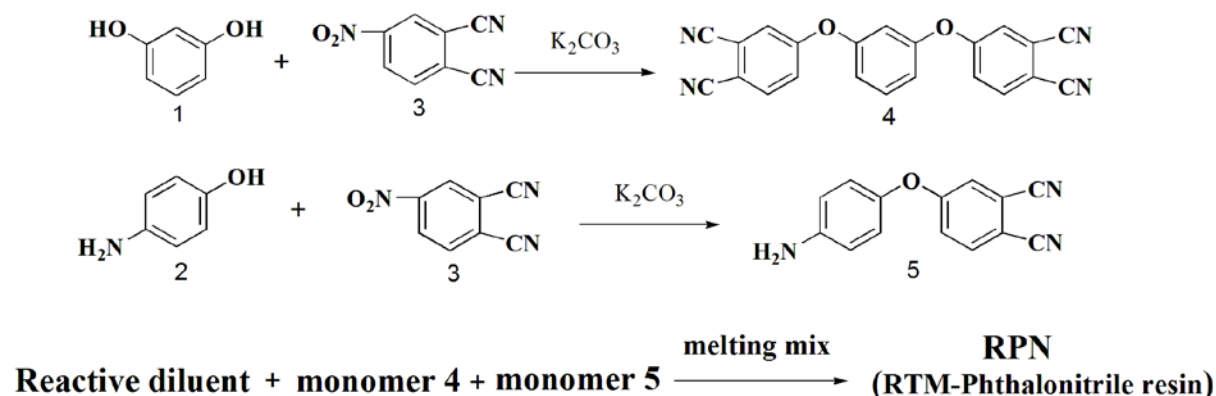


Figure 1. Synthesis route of monomers and modified phthalonitrile resins

2.2.1 Synthesis of monomer 4

A three-necked flask with a condenser, magnetic stirrer, thermometer and nitrogen inlet was added with 11.0 g (0.10 mol) resorcinol 1, 34.6g (0.20 mol) 4-nitrophthalonitrile 3, and 27.6g (0.20 mol) anhydrous potassium carbonate, and 180 ml of N, N-dimethylformamide (DMF). While stirring, the resulting mixture was heated at 85°C for 7h under an inert atmosphere. After cooling, the product mixture was poured into 600 ml of distilled water. The off-white solid 4 was collected by suction filtration and washed with water until the filtrate was neutral. After recrystallized from acetone and dried at 80°C for 8h in vacuum oven, 28.34g of product 1,3-bis(3,4-dicyanophenoxy)benzene 4 were isolated. Yield: 78%. M.p.: 185°C (determined by DSC). 1H NMR(400 MHz, DMSO- d_6 , δ): 7.54-7.56 (d,2Ar-H), 7.91 (s,2Ar-H), 8.11-8.13 (d,2Ar-H), 7.14 (s, Ar-H), 7.12-7.14 (d,2 Ar-H), 7.56-7.60 (dd, Ar-H).

2.2.2 Synthesis of monomer 5

The monomer 5 was synthesized in our lab, which has been previously reported [22].

2.2.3 Development of RTM-Phthalonitrile resin (DPNs)

Firstly, phthalonitrile blend was prepared by stirring the phthalonitrile monomer 4 into the viscous liquid phthalonitrile monomer 5 at 140°C under nitrogen atmosphere to form a homogeneous mixture. The blend was formulated with 1:1 molar ratios of the monomer 4 and monomer 5, which was the SPCN1010 as mentioned in the introduction and reported in SAMPE 2011 conference and exhibition. After SPCN1010 was developed, reactive diluents was added to the system with 5 wt%, 10 wt% or 30 wt% to form the RTM phthalonitrile resins, named DPN5, DPN10 and DPN30, respectively.

2.3 Preparation of cured RPN and RTM laminates on 2.5D fabric of carbon-glass hybrid

In order to evaluate thermal properties, the cured DPN was obtained by the following heating profile: 170°C/3h + 200°C/2h + 250°C/5h + 315°C/5h + 375°C/5h in an oven open to the air.

Laminates of DPNs were made by RTM using 2.5D fabric of carbon-glass hybrid. DPNs was injected into 2.5D fabric positioned in a steel mold using a high temperature injector machine (ISO JET piston10ht France). The mold containing the fabric was loaded into an oven, heated to 150°C, and held at 150°C for 1.5 hours prior to resin injection. The molten resin was used to infiltrate the fabric in the steel mold under 0.5MPa hydrostatic pressure during the entire process cycle. After the resin was injected at 150°C at a rate of 50cc/min, the mold was heated

in the following profile: 170°C/3h + 200°C/2h + 250°C/5h, then 315°C/5h + 375°C/5h for the laminate curing freely. The laminate was cut into specimens after cooled to room temperature, and tested for physical and mechanical properties.

2.4 Characterization method

¹H-NMR were recorded on a Bruker AV 400 spectrometer using DMSO-d₆ as solvent with respect to tetramethylsilane (TMS) as internal standard. Melt viscosity measurements was performed on a NDJ-7 Rotational Viscometer made in Shanghai Balance Instrument Factory. Differential scanning calorimetry (DSC) diagrams were recorded with Mettler-toledo DSC822e at heating rate of 10 °C/min under nitrogen atmosphere with flow rate of 50ml/min. Thermal stability was evaluated by thermogravimetry analysis (TGA) on Netzsch STA409PC at a heating rate of 10°C /min in atmosphere. RTM high temperature injector machine was ISO JET piston10ht made in France. Dynamic mechanical analysis (DMA) was performed on DMA 242c (Netzsch, Germany) at a fixed frequency of 1Hz with single cantilever mode and the oven was heated from 30°C to 500°C at a heating rate of 5°C/min in nitrogen atmosphere. The T_g was estimated from modulus vs. temperature plots obtained by dynamic mechanical analysis. The T_g was obtained from the onset of the decay in storage modulus in a plot of ln(modulus) vs. temperature. This technique underestimates T_g compared with other methods. Mechanical properties were measured on Instron Universal Tester Model 3365. Short beam shear strength values of the composites were measured according to ASTM D 2344. Flexural properties of the composites were measured by three-point bending test according to ASTM D 790-00.

3 Results and discussion

3.1 Study on processability by viscometer

Rotational viscometer was used to investigate meltability and processability of DPN. The study was carried out by heating DPNs to desired temperature, testing the viscosity change over time. As shown in table 1, viscosity measurements were recorded in the isothermal conditions of 130°C, 140°C or 150°C. DPN5 didn't have as much wide "processing window" as DPN10 and DPN30, owing to the lower containing of reactive diluents. The viscosity of both DPN10 and DPN30 maintained below 1Pa·s over 4 hours at 130°C or 140°C, which was greatly longer enough for RTM process. Especially, DPN30 had the lowest viscosity below 100mPa·s at 130°C and 140°C. The relatively low viscosity of the phthalonitrile resins at moderate temperatures is one key feature that advantageously affects their processing to a thermoset.

Modified resins	Viscosity [mPa·s] and meltable stability at certain temperature	
DPN5	450-500mPa·s for 3.5h at 140°C	<100mPa·s for 3h at 150°C
DPN10	450-530mPa·s >4h at 130°C	120-200mPa·s >4h at 140°C
DPN30	<100mPa·s >4h at 130°C	<100mPa·s >4h at 140°C

Table 1. Viscosity and "processing window" of different modified resins at certain temperature

3.2 Study on cure behavior by DSC

DSC technique was used to study the cure reaction of modified resins as shown in figure 2 and table 2. With increased the amount of reactive diluent, two endothermal peaks of modified resins became one, and DPN30 had the lowest melting transition temperature with the peak at about 130°C. For the exothermal peak, the cure temperature increased a little with the peak from 223°C to about 240°C. After adding reactive diluents into system, the enthalpy was increased compared with SPCN1010. With increasing the amount of diluents, the enthalpy decreased. DPN5 had the highest enthalpy of 185.1 J/g, and DPN30 had the lowest enthalpy of 170.3 J/g. The reason may be that more diluents reduced the reactivity of resin system.

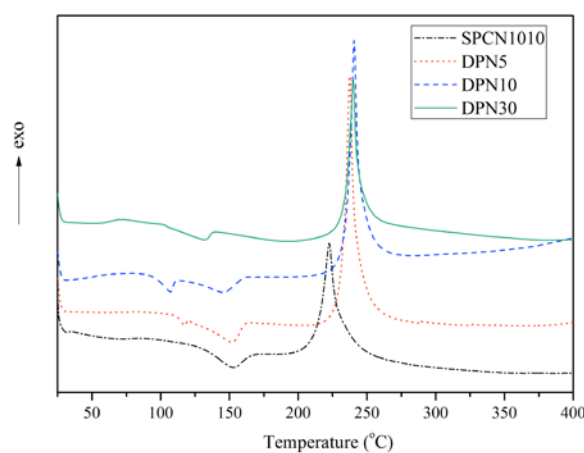


Figure 2. DSC curves of SPCN1010 and different modified resins

Modified resins	Cure peak temperature[°C]	Normalized[J/g]
SPCN1010	223	162.7
DPN5	238	185.1
DPN10	241	178.1
DPN30	240	170.3

Table 2. Characteristic data from DSC curves of different modified resins

3.3 Study on thermal properties

The thermal stability of cured DPNs was investigated by TGA under nitrogen atmosphere. The thermograms are shown in Figure 3 and the data are collected in table 3. The data revealed that after cure reaction the reactive diluents didn't affect the thermal properties. The cured DPNs had comparable or even a litter better thermal properties than cured SPCN1010, with 5% weight loss temperature above 530°C and high char yield over 73% at 900°C. High char yield indicated that DPNs can be used as high temperature ablation material probably.

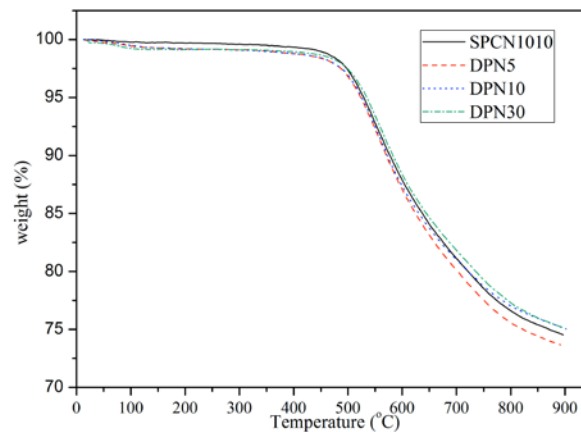


Figure 3. TGA curves of cured SPCN1010 and different modified resins

Modified resins	5% weight loss temperature	Char yield at 900°C
SPCN1010	528.7°C	74.4%
DPN5	528.9°C	73.7%
DPN10	530.7°C	75.1%
DPN30	539.7°C	75.1%

Table 3. Characteristic data from TGA curves of different modified resins in N₂

3.4 Mechanical properties of DPN30-2.5D fabric laminates

Based on the excellent processability and thermal properties, DPN30 was chosen to make composite according to section 2.3. The storage modulus (E') and the loss factor ($\tan\delta$) of cured DPN30-fabric composite were evaluated between 40 and 500°C in a nitrogen atmosphere using a DMA technique as shown in figure 4. After cured to 375°C for 5h, the E' of sample didn't commence to slowly decline until temperature increased up to 460°C and showed a $\tan\delta$ peak at 490°C. This illustrated DPN30 had so much high glass transition temperature.

For the RTM processing laminates of DPN30, the flexure properties and short beam shear strength of composite panels at room and elevated temperatures were summarized in Table 4. The test method is as followed: the sample was heated from room temperature to aim temperature and maintained 10 min when aim temperature was below 400°C (maintained 1 min when aim temperature was above 400°C). The flexure strength value was 371MPa at room temperature. Interestingly, the data was increased a little at 200°C and slightly declined at 300°C and maintained 29.6% and 26.9% at the test temperature of 400°C and 500°C, respectively. The short beam shear strength of panels was 60.9MPa at room temperature. Upon to 400°C and 500°C, the samples still had strength retention of about 31.0% and 22.5%, respectively. It should be noted worthily that the composite had flexure strength of 38.3MPa and short beam shear strength of 5.95MPa even up to 600°C, which was amazing for organic

materials. These demonstrated that the DPN30/2.5D fabric composite retained very good mechanical properties at elevated temperatures.

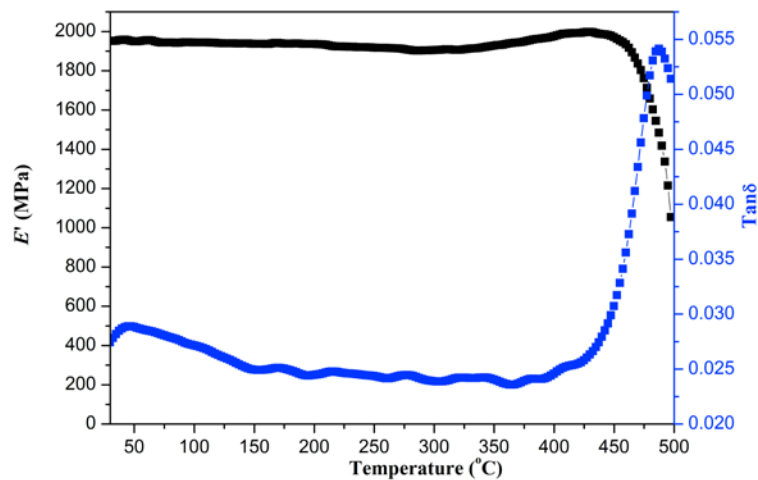


Figure 4. DMA curves of cured DPN30 composite

DPN30 composite	flexural strength [MPa]	flexural modulus [GPa]	short beam shear strength [MPa]
Room temperature	371	22.3	60.9
100°C	368	22.4	51.8
200°C	401	21.6	52.9
300°C	341	24.2	31.1
400°C	110	4.41	18.9
500°C	99.8	9.91	13.7
600°C	38.3	2.55	5.95

Table 4. Mechanical properties of DPN30/2.5D fabric of carbon-glass hybrid composite

4 Conclusions

A series of phthalonitrile resins based on modification of SPCN1010 were developed with adding reactive diluents in different weight ratio. Both DPN10 with 10wt% diluents and DPN30 with 10wt% diluents had better processability than DPN5 according to rotational viscometer test. They can maintain low viscosity below 1 Pa.s over 4 hours, which was greatly suitable for RTM process. DPNs had similar cure behavior from DSC curves and the cure peak temperature was a little higher than the one of SPCN1010. After cured to 375°C, cured DPNs had high thermal stability with 5% weight loss temperature above 530°C in nitrogen and high char yield over 73%. Furthermore, DPN30-2.5D fabric composite fabricated by RTM had a glass transition temperature (T_g) at 460°C and retained very good mechanical properties at elevated temperatures. Upon to 400°C and 500°C, the flexure strength value maintained 29.6% and 26.9% to the value of room temperature, respectively, and the short beam shear strength of panels had retention of about 31.0% and 22.5%, respectively. Even up to 600°C, DPN30 composite had flexure strength of 38.3MPa and short beam shear strength of 5.95MPa. All above showed DPNs may be a good candidate for high performance polymeric materials.

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