

STUDY ON A MODIFIED PHTHALONITRILE RESIN SYSTEM SUITABLE FOR PREPREG PREPARATION

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ABSTRACT

In order to improve the processability of phthalonitrile resins without sacrificing their thermal properties, a modified phthalonitrile resin system with good tack at room temperature was developed by the blends between the reacted diluents 3-aminophenylacetylene and phthalonitrile monomers. The non-isothermal curing kinetics and thermal properties of the modified phthalonitrile resin named PN1001 and corresponding composites were studied. Results showed that the obtained phthalonitrile resin system was suitable for hot-melt prepreg preparation and had high temperature resistance ($T_g=440^\circ\text{C}$) and good thermal stability. Its corresponding carbon fiber reinforced composites owned superior mechanical properties at room temperature and exhibited good mechanical property retention at elevated temperature as high as 350°C .

1 INTRODUCTION

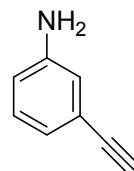
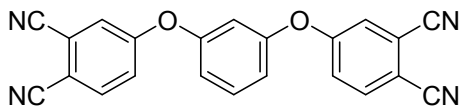
Much high-temperature resistant polymer have been drawn more and more attention and applied in aerospace industries in the form of composite matrices[1-3]. Among which, phthalonitrile-based polymers, whose cure reaction is not accompanied by evolution of volatile byproducts compared to that of polyimides, have potential to be used over 350°C [4,5]. However, phthalonitrile resins have some disadvantages on processability due to the high-melting temperature of phthalonitrile monomers, in the meanwhile modification on decreasing melting point usually leads to destroy their heat-resistance. Accordingly, it will make much sense to improve the processability of phthalonitrile resins without sacrificing their thermal properties especially in engineering application. Furthermore the curing condition may significantly affect the final performance of the cured products, it is also necessary to learn about the curing kinetics of the resin systems prior to application.

This paper concerns processability, the cure kinetics and thermal properties of the modified phthalonitrile resin suitable for hot-melt prepreg, basic data on composite mechanical properties both at room temperature and 350°C , finally fracture morphology of fiber reinforced composite was also studied.

2 EXPERIMENTAL

2.1 Materials

Phthalonitrile monomers, 4,4'-bis(3,4-dicyanophenoxy)bisphenyl(A) and 1,3-bis(3,4-dicyanophenoxy)benzene(B) were supplied by Chengdu Keda Sheehan New Materials Co., Ltd., the 3-aminophenylacetylene (C) was purchased from Natong Synasia Co., Ltd. The chemical structures are shown in Figure 1.



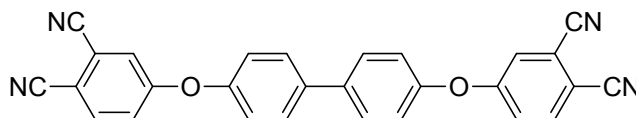


Fig. 1: Structure of phthalonitrile monomers and modification

2.2 Preparation and Fabrication

The modified phthalateslontrile resin system was prepared by adding the reacted diluents to the melted mixture of phthalonitrile monomers. After vigorous stirring for 60 min at 160°C, the reaction mixture was quenched to room temperature to form a B-stage prepolymer nominated PN1001 and could be stored indefinitely under ambient conditions.

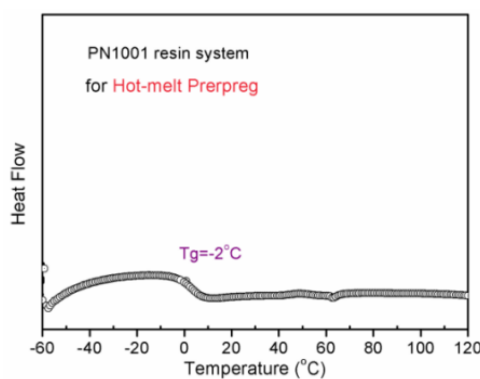


Fig. 2: DSC curve with 10 °C/min to test Tg of uncured PN1001 resin system

Prepreg tape was formulated from prepolymer using a hot-melt impregnation process. Toray T800H-12K carbon fiber and PN1001 resin were used. Unidirectional components panels were fabricated in an autoclave as follows: 170°C/1h+250°C/2h+325°C/2h+350°C/2h under 0.6MPa. The quality of the composite panels were determined by ultrasonic examination, the result revealed the composite had good quality. For metallographic analysis, small sections of the panel were embedded in an epoxy mount and polished sequentially using sandpaper.

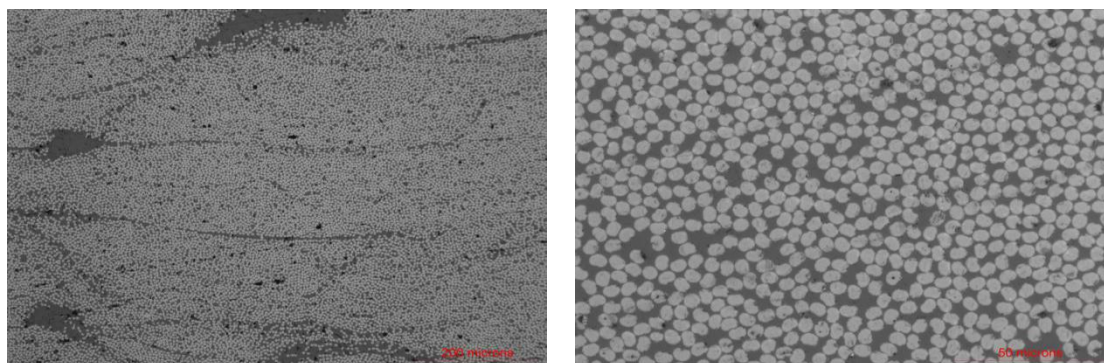


Fig. 3: Metallographic analysis of T800/PN1001 composites

2.3 Measurements

Parallel plate rheological measurement (Temperature sweep) was conducted using an Anton Paar MCR 301 rheometer from 25 to 250°C at the heating rate of 0.5°C/min under air atmosphere. The gap size between the plates, frequency and strain were respectively set at 1 mm, 1 Hz and 0.1%.

The non-isothermal reaction at 5, 10, 15 or 20 °C/min were monitored by a Mettler-Toledo DSC1 under N₂ atmosphere. Note here that in the isothermal experimental, the sample was rapidly cooled to 50 °C after the first isothermal run, and then immediately heated to 360°C with a heating rate of

10°C/min to determine the residual reaction heat ΔH_{res} . Thus the relationship between the fractional conversion α and reaction time t for the isothermal cure can be determined by Eq. (1) [6]:

$$\alpha = \frac{\int_0^t (dH/dt) dt}{\Delta H_{iso} + \Delta H_{res}} \quad (1)$$

Where dH/dt is the DSC heat flow rate and ΔH_{iso} is the isothermal reaction heat.

3 RESULTS AND DISCUSSION

3.1 Rheological measurement

The non-isothermal curing behavior of PN1001 was firstly investigated by the parallel plate rheological measurement, and the variation of complex viscosity with time is shown in Fig. 4. It could be seen that with the increase of temperature, the complex viscosity of PN1001 first decreased, then reached a plateau, at which the viscosity kept 0.5 Pa.s. The complex viscosity was about 30000 Pa.s at 30°C, indicating that the T800/PN1001 prepreg had good tackiness at room temperature. However, in the relatively high reaction temperature stage (e.g. 175°C), the complex viscosity increased steadily due to rapid crosslinking reaction of the modified phthalonitrile resin, which also indicated that the addition of 3-aminophenylacetylene could obviously hasten the curing processing of phthalonitrile resins.

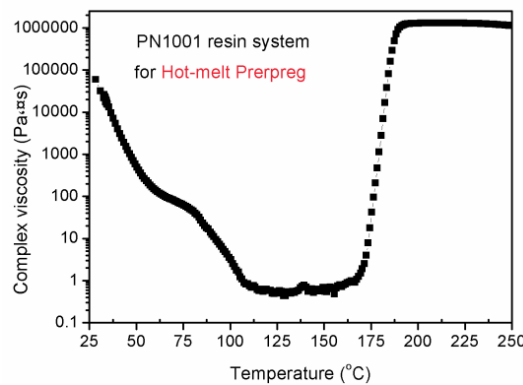


Fig.4: Variation of complex viscosity versus temperature for PN1001

3.2 Non-isothermal curing reaction of PN1001

The non-isothermal DSC curves of PN1001 were presented in Fig. 5. In the case of high heating rate there is not enough time for completing the curing reaction; therefore the DSC curve will shift to a high temperature to compensate for the reduced time [8]. Assuming that the reaction exotherms are directly proportional to the conversion of the curing reaction, one can express the curing reaction rate $d\alpha/dt$ by Eq. (2) [7]:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} = k(T)f(\alpha) \quad (2)$$

Where ΔH_0 is the total reaction heat, $k(T)$ is the temperature-dependent reaction rate constant, and $f(\alpha)$ is the function of conversion. In general, $k(T)$ can be represented through the Arrhenius equation [7]:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Where A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature.

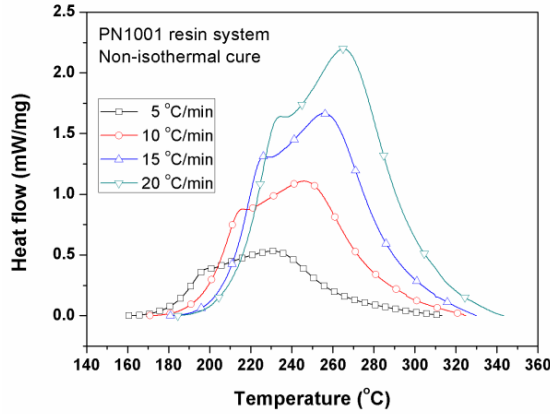


Fig. 5: Non-isothermal DSC curves of PN1001 system

For non-isothermal conditions, the value of apparent activation energy can be determined by various methods. In this paper, the Flynn-Wall-Ozawa [Eq.(4)] [8] method was used to reveal the dependency of apparent activation energy on fractional conversion, and then the average value of apparent activation energy was calculated.

$$\ln \beta = Const. - \frac{1.052E_{\alpha}}{RT_{\alpha}} \quad (4)$$

Where β is the heating rate, and E_{α} and T_{α} are the apparent activation energy and absolute temperature at the fractional conversion of α , respectively.

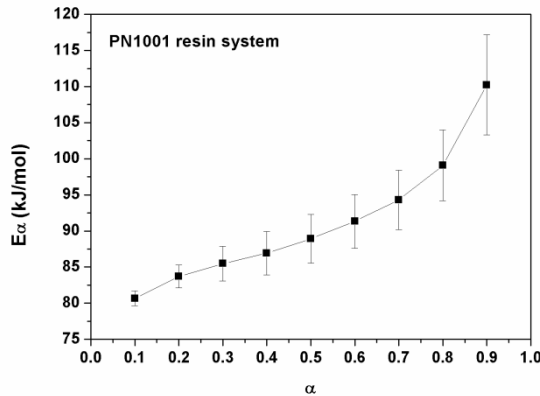


Fig. 6: The E_{α} - α dependency for the non-isothermal cure of PN1001

From Eq. (4) one can find that a plot of $\ln\beta$ versus $1/T_{\alpha}$ values obtained from the non-isothermal experimental data at the same fractional conversion will result in a straight line with a slope of $-1.052E_{\alpha}/R$, and then the value of E_{α} can be calculated by multiplying the slope value and $-R/1.052$. The E_{α} - α dependency for the non-isothermal cure of PN1001 is shown in Fig.6. As can be seen, E_{α} varies markedly with α especially at the terminated stage of the non-isothermal curing processing reaction, indicating that the curing reaction may be complex. It can be observed clearly that the value of E_{α} tends to increase with increasing the reaction extent, the increasing E_{α} - α dependency may be attributed the propagation process of the polymer chain which may lead to the heightened energetic barrier for the subsequent curing reactions. The average value of the apparent activation energy calculated from the E_{α} - α dependency for the non-isothermal cure of PN1001 is 91.2 kJ/mol.

3.3 Thermal Properties of cured PN1001 phthalonitrile resin system

Fig. 7 showed the DMA curves of PN1001 resin system. The glass transition temperatures (T_g , the $\tan\delta$ peak temperatures) and storage modulus at 350°C (E'_{350}) were listed in Table 1, indicating that the obtained phthalonitrile resin system had high temperature resistance. There are two factors which affect the glass transition temperature. One is the stiffness of phthalonitrile polymer chain, the other is the increased crosslinking density due to the introduction of reacted 3-aminophenylacetylene.

The thermal stability of the cured PN1001 was investigated by TGA. The thermogram curves were depicted in Figure 8. The decomposition temperature (T_d) was 485°C and residual weight at 1000°C was as high as 75%, which indicated the excellent thermal stabilities of cured PN1001.

	T_g^a (°C)	E'_{350}^b (GPa)	T_d^c (°C)	W_{1000}^d (%)
Cured PN1001	440	6.3	485	75

^a Peak temperature of $\tan\delta$; ^b Storage Modulus at 350°C;
^c Onset decomposition temperature; ^d Char at 1000°C;

Table 1: The thermal properties of T800/PN1001

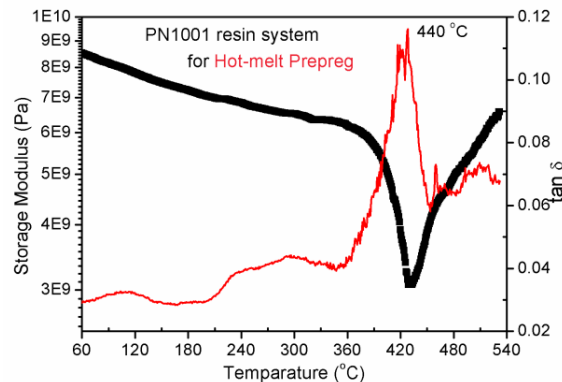


Fig. 7: DMA curves for the cured PN1001

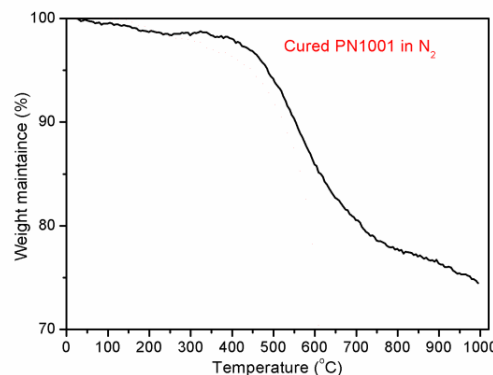


Fig. 8: TGA curves for the cured PN1001 in N_2

3.4 Mechanical Properties and fracture morphology of T800/PN1001 fiber reinforced composites

The mechanical properties of T800/PN1001 composites both at room temperature and 350°C were listed in Table 2. It could be clearly seen that the corresponding composite owned superior mechanical properties and exhibited good mechanical property retention at elevated temperature as high as 350°C.

0° Tension Strength(MPa)	2490	-	-
0°Flexure Strength(MPa)	1630	1100	985
Short Beam Shear Strength (MPa)	80.0	50.4	46.3

Table 2: The mechanical properties of T800/PN1001

The fracture surface of the fiber reinforced composites was shown in Fig. 9. As can be seen that the carbon fiber and modified phthalonitrile resin were homogeneously distributed and well bonded, which was advantageous to optimize the composite material performance.

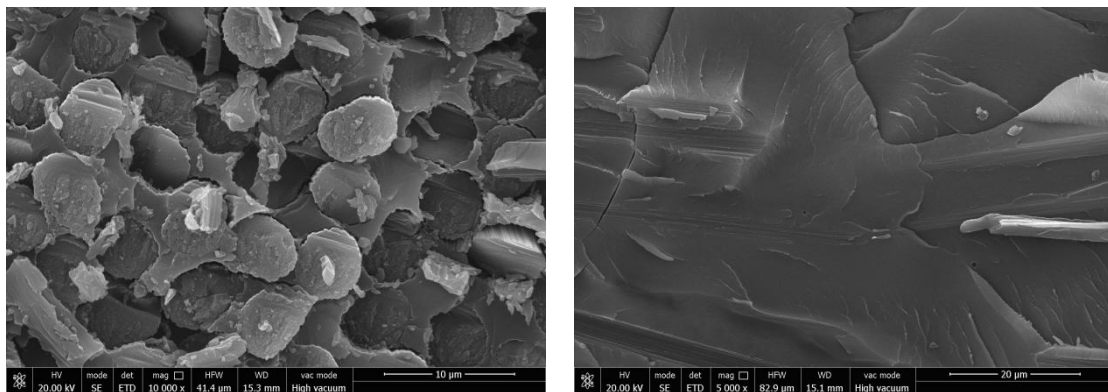


Fig. 9: Fracture Micromorphology of fiber reinforced T800/PN1001 composites

4 CONCLUSIONS

A modified phthalonitrile resin system suitable for hot-melt prepreg (PN1001) was prepared. The addition of 3-aminophenylacetylene could improve the processability as well as obviously hasten the curing processing of phthalonitrile resins without scaring excellent thermal properties. The non-isothermal curing study revealed that E_a varies markedly with α probably due to the complex curing mechanism and the average value of the apparent activation energy was 91.2 kJ/mol. The corresponding carbon fiber reinforced composites owned superior mechanical properties and exhibited excellent mechanical property retention at elevated temperature as high as 350°C.

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