



# Curing kinetics, thermal and adhesive properties of phthalonitrile/aromatic diamine systems

Caizhao Liu<sup>1,2</sup> · Mingming Sun<sup>2</sup> · Bin Zhang<sup>1,2</sup>  · Xugang Zhang<sup>2</sup> · Gang Xue<sup>1,2</sup> · Xiwen Zhang<sup>1</sup>

Received: 23 July 2019 / Accepted: 7 December 2019 / Published online: 16 December 2019  
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## Abstract

The present work reports on the synthesis of an easily processable phthalonitrile monomer (BBPN) with isobutyl segment. The effect of various curing agents on curing behaviors, thermal and adhesive properties of BBPN has been evaluated. The novel phthalonitrile monomer was synthesized through nucleophilic substitution of 2,2-bis(4-hydroxyphenyl)butane (BPB) and 4-nitrophthalonitrile, and its chemical structure was characterized with FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR analyses. Four different aromatic diamines derived from different catalytic activities such as *p*-phenylenediamine (*p*-PD), *m*-tolidine (*m*-TB), *o*-tolidine (*o*-TB), and 2,2'-bis(trifluoromethyl)benzidine (TFMB) were used as curing agents. The curing kinetics of BBPN/aromatic diamine samples were investigated by non-isothermal differential scanning calorimetry (DSC) at different heating rates. The average activation energy was calculated based on Kissinger's and Ozawa's methods varied in the range of 66.61–79.00 kJ mol<sup>-1</sup>. The thermal properties of the obtained polymers were investigated by dynamic mechanical thermal analysis (DMA) and thermogravimetric analysis (TGA). Compared to other three systems, the cured BBPN/*p*-PD exhibited better thermal stability and higher glass-transition temperature ( $T_g$ ), suggesting its higher degree of cross-linking. Moreover, the BBPN/diamine systems were used to bond aluminum sheet, and the average values of lap shear strengths were in the range of 13.8–19.6 MPa at room temperature and 9.2–11.5 MPa at 300 °C, respectively.

**Keywords** Phthalonitrile · Kinetics · Thermal properties · Thermosets · Adhesive

## Introduction

Over the past few decades, the use of high performance polymeric materials has shown a rapid increase due to the development of aerospace technology. As a typical high-temperature resistant polymer, phthalonitrile was initially developed at U.S. Naval Research Laboratory [1]. Phthalonitrile monomers can be simply prepared from 4-nitrophthalonitrile and commercially available phenols or their

derivatives in the presence of weak base catalyst [2–4]. Consequently, the chemistry of phthalonitrile synthesis provides a wide range of molecular design flexibility. They are allowed to be thermally polymerized and to form aromatic heterocyclic structures such as triazine, phthalocyanine, dehydrophthalocyanine, and isoindoline [5–7]. Due to their outstanding thermo-oxidative stability [8], excellent mechanical properties [9], high  $T_g$ , superior flame resistance and low water absorptivity [10], phthalonitriles have been widely applied in the form of electronic conductors, carbon precursors as well as in composite productions [11–13].

However, the traditional phthalonitriles have undesirably high melting point ( $T_m$ ) and poor processability, and it is difficult to process them into suitable form. To address these issues and overcome the associated disadvantages, dual-function has been approved to be a well-established approach [14, 15]. Recently, many amine- and hydroxyl-functional phthalonitrile monomers with low  $T_m$  were investigated [16–18]. Zhou et al. created a series of phthalonitriles containing allyl groups and the dual-functional monomers melt at a lower temperature between 61 and 98 °C [19]. The

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s13726-019-00775-7>) contains supplementary material, which is available to authorized users.

✉ Bin Zhang  
zhangbin\_hipc@126.com

<sup>1</sup> College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, Heilongjiang, People's Republic of China

<sup>2</sup> Institute of Petrochemistry, Heilongjiang Academy of Sciences, Harbin 150020, Heilongjiang, People's Republic of China