

Study on cure reaction of the blends of bismaleimide and dicyanate ester

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Abstract

In this work, the cure reaction of the blends of bisphenol A dicyanate ester (BADCy) and 4,4'-bismaleimidodiphenylmethane (BMI) was investigated by using DSC, in situ FTIR, DMA and generalized 2D correlation analysis. The results clarified that there existed different kinds of cure mechanism in the blends of bismaleimide and dicyanate ester. In non-catalyzed blends, the dicyanate ester and bismaleimide cured independently and formed two kinds of network: polycyanurate and polybismaleimide. A cyanate curing catalyst accelerated the cure of dicyanate ester but did not change the independent cure mechanism of two components. Moreover a commercial ring closure catalyst, which was usually used in the synthesis of bismaleimide, resulted in the co-reaction between two components and formed a homogeneous network. Thus, the cure mechanism of the blends of dicyanate ester and bismaleimide was related to the catalyst presented in the blends systems.

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1. Introduction

Bismaleimide resins, as a kind of high-performance materials, have received more and more interest because of their good thermal stability, low water absorption and good retention of mechanical properties at high temperatures. However, due to their highly crosslinked structures, bismaleimide resins are extremely brittle and thus are often modified for application [1–4]. Cyanate esters, on the other hand, have very good toughness. Hence the cured blends of bismaleimide and dicyanate ester would have excellent physicochemical performance: thermal characteristics from bismaleimide and toughness from dicyanate ester. The commercial blends formulations of bismaleimide–cyanate, known as B–T resins, are already introduced [5,6]. Up to now several patented B–T resins formulations have been applied as engineering materials in electric industry, reinforced plastics and aircrafts [7,8].

However, the cure mechanism of the blends of bismaleimide and dicyanate ester is highly controversial and sometimes conflicting, which is still not well established and cannot support all experiment phenomena.

Some researches believed that the resultant polymer matrix is an interpenetrating network (IPN) because the resultant blends had two T_g s, which implied the microphase separation structure [9–12]. Barton et al. found no evidences for any such product as pyrimidine and/or pyridine structures by using model compound and heteronuclear NMR [11,12]. Enoki and Takeda found no evidence for co-reaction between cyanate groups and maleimide groups by FTIR and ^{13}C NMR techniques [13]. Nair found the evidence of two-stage cure reaction of the components of the blends by DSC and confirmed them by DMA [14]. These experiment phenomena have led to the conclusion that in the blends the dicyanate ester and the bismaleimide cured independently and formed IPN.

On the other hand, Hong et al. studied the reaction kinetics of bis(4-maleimido phenyl)methane and bisphenol A dicyanate by DSC and FTIR and found the cure mechanism was related to the blends composition [15]. Rong-Hsien Lin et al. investigated the cure reactions of 4,4-bismaleimidodiphenylmethane (BMI) associated with 1,10-bis(4-cyanatophenyl)ethane and with bisphenol A dicyanate ester (BADCy) by using FTIR and DSC and found that in non-catalyzed blends systems, co-reactions between the dicyanate ester and bismaleimide always occur [16,17].

It should be pointed out that the above-mentioned systems were studied with or without adding a cyanate curing catalyst, such as copper-acetylacetonate, nonylphenol and dibutyl tindilaurate [9–17]. However, the ring closure and dehydration catalyst, which were always used in the synthesis of

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bismaleimide, such as acetic anhydride, sodium acetate, phosphoric acid and *p*-toluene sulphonic acid, etc. [18–26], may present in the blends and will affect the cure reaction mechanism of the blends.

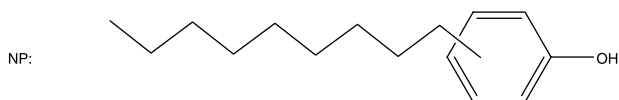
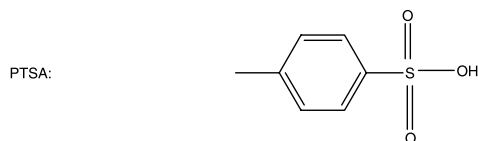
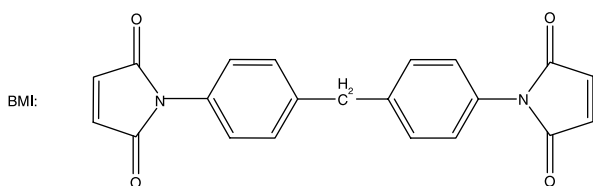
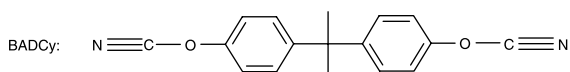
To clarify the cure mechanism of the blends of bismaleimide and dicyanate ester, we studied the cure reaction of the blends of BMI and BADCy by using DSC, in situ FTIR, DMA, and generalized 2D IR correlation analysis.

To avoid the possible disturbances came from the substances presented in the component, in this work the BMI and BADCy were purified before used. Then the nonylphenol (a cyanate curing catalyst) and the *p*-toluene sulphonic acid (a ring closure catalyst, which was usually used in the synthesis of bismaleimide) were added into the blends of bismaleimide and dicyanate ester to investigate the effect of catalyst on the cure mechanism.

2. Experimental section

2.1. Materials

4,4-Bismaleimidodiphenylmethane (BMI, Aldrich Chemical Co.) was purified through column chromatography using silica gel as the column support and eluting with 90:10 dichloromethane/ether mixtures and then depositing with methanol. Bisphenol-A dicyanate (BADCy, Beijing Aeronautical Manufacturing Technology Research Institute) was thrice recrystallized from cyclohexane before used. *p*-Toluene sulphonic acid (PTSA, Shanghai Chemical Reagent Co. Ltd) and nonylphenol (NP, Aldrich Chemical Co.) were used as purchased.



2.2. Sample preparation

BMI and BADCy, with/without catalyst (according to Table 1), were homogeneously mixed by dichloromethane. Residual solvent was removed under vacuum at 60 °C for at

Table 1
Composition of the blends of bismaleimide and dicyanate ester

Blends	Components	Catalyst
BC-0	BMI:BADCy = 1:1 (molar ratio)	None
BC-1	BMI:BADCy = 1:1 (molar ratio)	NP
BC-2	BMI:BADCy = 1:1 (molar ratio)	PTSA

least 24 h after most of solvent was evaporated at room temperature.

2.3. Differential scanning calorimetry (DSC)

Small quantities of sample were scanned in a differential scanning calorimeter (Perkin–Elmer DSC-7) with an indium standard. A stream of N₂ at a flow rate of 20 ml/min was used to protect the DSC cell.

2.4. Dynamic mechanical analysis (DMA)

Glass cloth with the dimension 6 × 1 cm² were impregnated with the blends at the temperature of 140 °C. Then they were put into two thick metallic platens and cured by programmed heating as follows: 150 °C/2 h + 180 °C/2 h + 230 °C/1 h. Dynamic mechanical analysis was performed in the dual-cantilever bending mode, using a Netzsch DMA 242 apparatus at the heating rate of 3 °C/min and the frequency of 5 Hz.

2.5. Fourier-transform infrared spectroscopy (FTIR)

The powder sample was put and heated at 140 °C between two NaCl pellets till the powder melted and became transparent. A Nicolet 470 FTIR spectrometer equipped with a temperature-controlled sample holder in a N₂ atmosphere was used. Cure reaction proceeded at requested temperature in the FTIR cell. The in situ FTIR Spectra were obtained at constant temperature in an optical range of 600–4000 cm⁻¹ by averaging 32 scans.

2.6. Two-dimensional (2D) correlation analysis

Spectra at equal time intervals in certain wavenumber ranges were selected for 2D correlation analysis by using the software matlab. Time-averaged reference spectrum was shown at the side and top of the 2D correlation maps for comparison.

3. Results and discussion

It is well known that if the cured blends were homogenous, they would have one glass transition, otherwise two glass transitions. DMA is an effective means to detect the glass transition and could provide the information whether the cured blends include two kinds of network, i.e. the fundamental results of the effect of catalyst on the cure mechanism.

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