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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.

Keywords: Bismaleimide; Dicyanate ester; Generalized 2D correlation analysis

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_gs, 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.

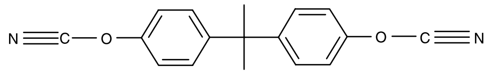
To avoid the possible disturbances came from the substances presented in the component, in this work the BMI and BADCy were purified before used. Then the nonylphenol (a cyanate curing catalyst) and the *p*-toluene sulphonic acid (a ring closure catalyst, which was usually used in the synthesis of bismaleimide)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

2. Experimental section

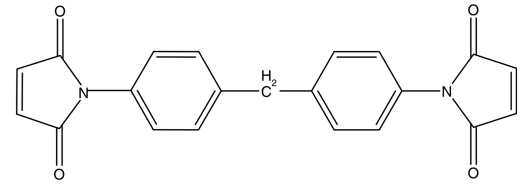
2.1. Materials

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.

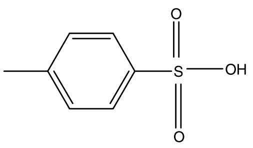
BADCy:



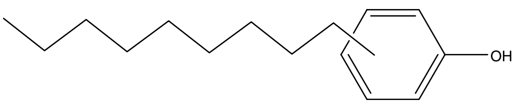
BMI:



PTSA:



NP:



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

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

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 N_2 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 cm^2 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 N_2 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.

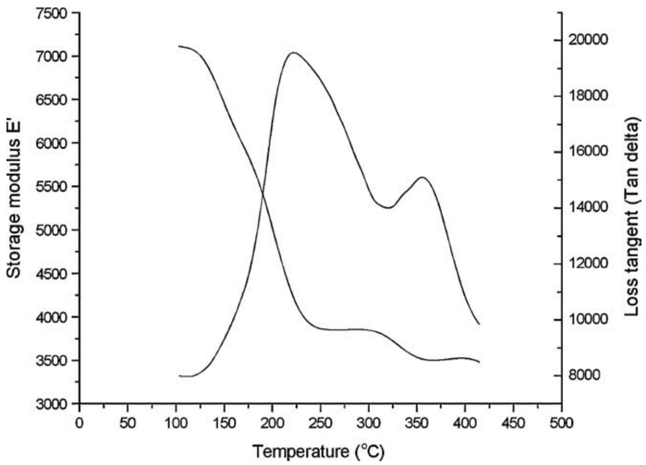


Fig. 1. The dynamic mechanical analysis of cured BC-0.

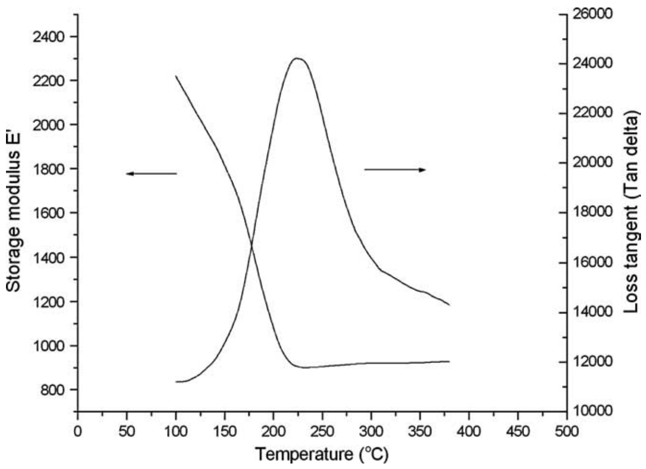


Fig. 3. The dynamic mechanical analysis of cured BC-2.

3.1. DMA analysis

The DMA curves of the temperature dependence of tan δ and storage modulus E' of the cured blends of BC-01, BC-1 and BC-2 are shown in Figs. 1–3. From the dynamic mechanical spectra, it is observed that the cured BC-0 (Fig. 1) exhibits well-defined dynamic mechanical damping peaks centered at 224 and 355 °C, which are ascribed to the glass transitions of polycyanurate and polybismaleimide, respectively [9]. Corresponding temperatures for BC-1 are 218 and 351 °C in Fig. 2. In contrast, only one dynamic mechanical damping peak at about 245 °C is observed in cured BC-2 (Fig. 3).

Two glass transitions undoubtedly confirmed that the cured BC-0 and cured BC-1 included two kinds of network. However, one single glass transition in cured BC-2 may indicate two possibilities: (a) a homogeneous network; (b) two kinds of network with small particle size. To further study the cure reaction, all blends were studied by DSC.

3.2. Cure characterization by DSC

Fig. 4 shows the DSC thermogram for the blends of BMI/BADCy at a heating rate of 10 °C/min. Both BC-0 (Fig. 4(A)) and BC-1 (Fig. 4(B)) show two obvious exothermic peaks. Since, the cure exothermic peak of pure BADCy is over 250 °C and the cure of pure BMI occurs just after the melting temperature (about 158 °C), the cure exothermic peaks of two pure components do not overlap. Two obviously separated exothermic peaks in BC-0 and BC-1 implied that two components possibly were cured independently: the peak at low-temperature was attributed to the cure of BMI and the peak at high-temperature was attributed to the cure of BADCy. The first cure reaction in BC-0 starts at 181 °C with a maximum at 201 °C and the second cure reaction starts at 235 °C with a maximum at 292 °C. Corresponding temperatures for BC-1 are 176, 216, 251 and 281 °C respectively. The DSC thermogram of BC-1 (Fig. 4(B)) also shows the cure reaction of BADCy is promoted by adding NP and the exothermic peak shifts to lower temperature compared with BC-0.

However, the DSC thermogram of BC-2 (Fig. 4(C)) is very different from BC-0 to BC-1. Fig. 4(C) shows only one exothermic peak in BC-2 that starts at 221 °C and reaches a maximum at 274 °C.

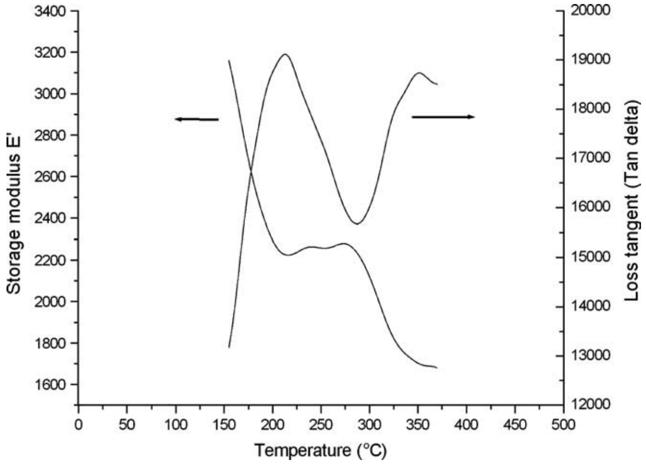


Fig. 2. The dynamic mechanical analysis of cured BC-1.

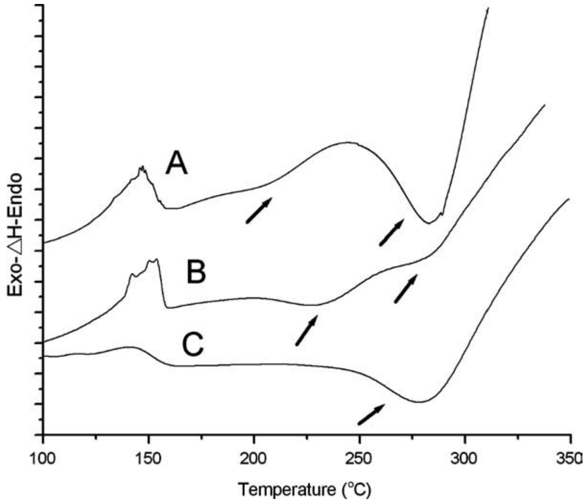


Fig. 4. DSC thermograms at a heating rate of 10 °C/min: (A) BC-0, (B) BC-1, (C) BC-2.

Table 2
Cure characteristics of BC-0, BC-1 and BC-2

Sample	T_p[a]	Activation energies (kJ/mol)
BMI	202	108
BADCy	308	89
BC-0		
Low-temperature peak	201	152
High-temperature peak	292	126
BC-1		
Low-temperature peak	216	148
High-temperature peak	281	111
BC-2	274	81

[a] Exothermic maximum (T_p) was determined DSC measurements at heating rate 10 °C/min.

Furthermore, the cure reaction activation energies were investigated by DSC. According to the Kissinger equation [27]:

$$-\ln\left(\frac{\Phi}{T_p^2}\right) = \ln\left(\frac{E}{R}\right) - \ln(An) - (n-1)\ln(1-\alpha)_p + \frac{E}{RT_p}$$

where φ is the heating rate, T_p is the temperature of the exothermic peak, E_a is the activation energy, and R is the gas constant. The activation energies of the cure reaction for BC-0, BC-1 and BC-2 were shown in Table 2.

For discussion, Table 2 also lists the cure reaction activation energies of the BMI and BADCy. It shows the cure reaction activation energy of BMI and BADCy in blends is remarkably higher than pure BMI and BADCy. Meanwhile, the cure reaction activation energy of BADCy in BC-1 is lower than that of BC-0, which is in agreement with Brown's previous studies that the hydrogendonating catalyst will decrease the cure activation energy of cyanate [28]. Furthermore, only one exothermic peak exists in BC-2 and the cure activation energy is lower than pure BMI and BADCy.

Although DSC results illustrated that two kinds of cure reaction occurred in BC-0 and BC-1, were two cure reactions really related to the cure of bismaleimide and the cure of dicyanate ester? Moreover, one exothermic peak in BC-2 may not simply suggest only one cure reaction occurred. Was it possible that the cure exothermic peak of dicyanate ester overlapped the cure exothermic peak of bismaleimide due to the catalyst PTSA? To further clarify those questions, FTIR spectroscopy was used to analyze the cure reaction of the blends.

3.3. FTIR analysis

The FTIR spectra of BC-0, BC-1 and BC-2 during isothermal curing at temperature of 200 °C are shown in Figs. 5–7. The absorption peak at 823, 1558 and 2267/2237 cm^{-1} were attributed to the out-of plane bending vibration of the maleimide =C–H in bismaleimide, the vibration of triazine ring in polycyanurate and the vibration of cyanate group in dicyanate ester, respectively [29].

The FTIR spectra of BC-0 (Fig. 5) and BC-1 (Fig. 6) show that the consumption of the cyanate group (2267 and 2237 cm^{-1}) is accompanied with the formation of triazine ring (1558 cm^{-1}), which suggested that dicyanate ester reacted and converted into polycyanurate. Meanwhile, the absorption of maleimide (823 cm^{-1}) gradually consumed, illuminating the cure of BMI and the formation of polybismaleimide. The FTIR results further confirmed that two kinds of reaction occurred in BC-0 and BC-1, which was in agreement with the DSC results.

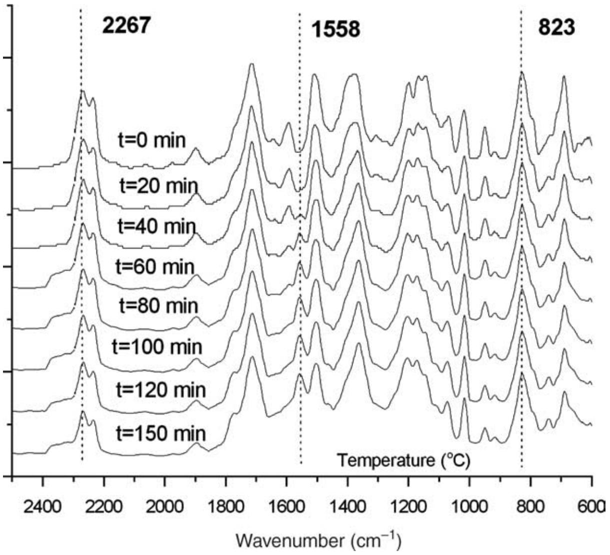


Fig. 5. FTIR spectra of BC-0 curing at the temperature of 200 °C.

However, the FTIR spectrum of BC-2 (Fig. 7) is different from BC-0 and BC-1: the consumption of cyanate group (2267 and 2237 cm^{-1}) and the consumption of maleimide (823 cm^{-1}) are not accompanied with the formation of triazine ring (1558 cm^{-1}), which suggested that the BADCy reacted but did not converted into polycyanurate. Combined with DSC result of BC-2 (Fig. 4(C)), it was assumed that the co-reaction between two components might be occurred and formed a new kind of network.

To further understand the cure reaction in the blends of BC-2, it was necessary to investigate the reaction sequence of cyanate group and bismaleimide.

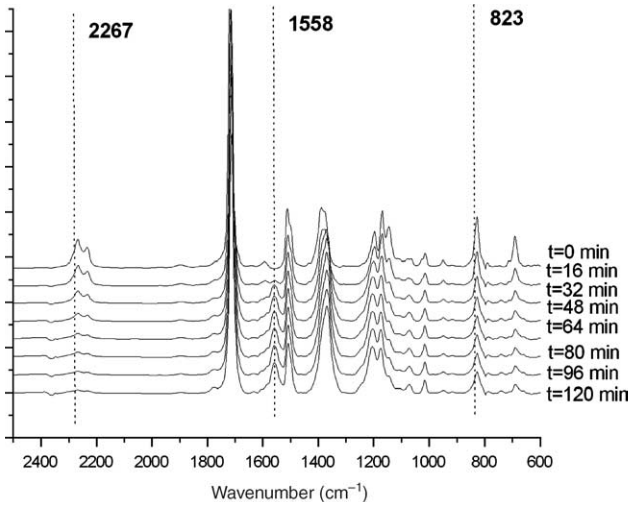


Fig. 6. FTIR spectra of BC-1 curing at the temperature of 200 °C.

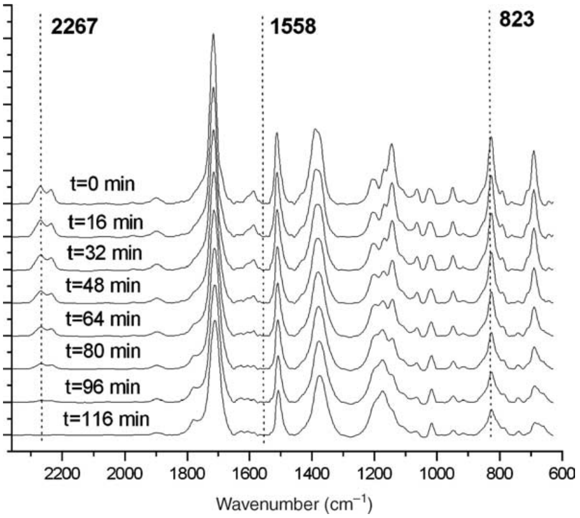


Fig. 7. FTIR spectra of BC-2 curing at the temperature of 200 °C.

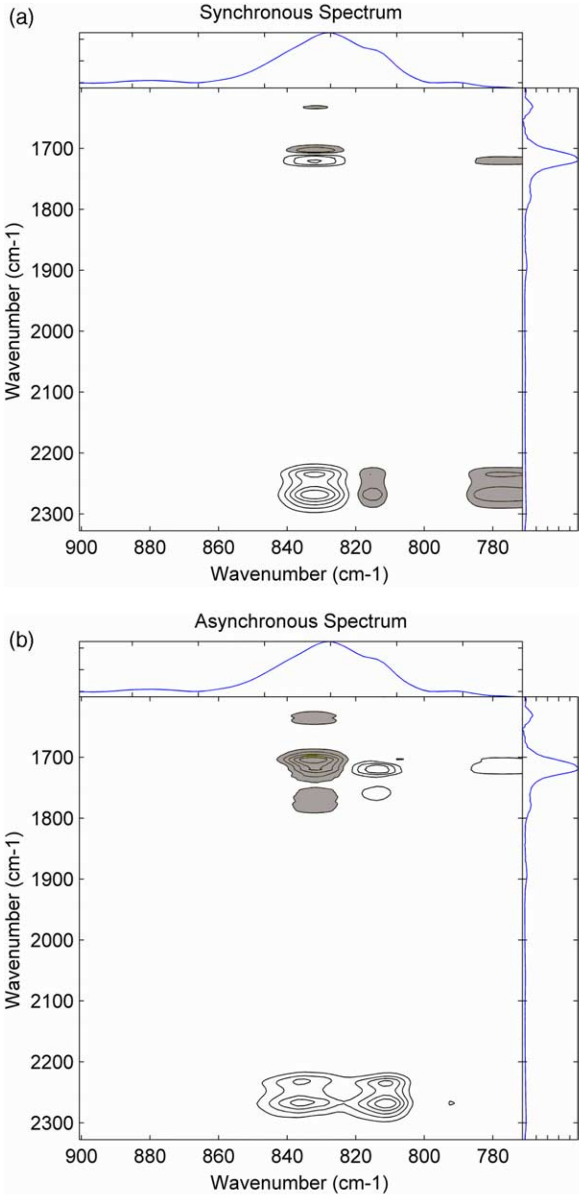
3.4. 2D correlation analysis of FTIR spectra

Since, the absorptions of maleimide (823 cm^{-1}) overlapped with the absorptions of other –C–H group, the change of the absorptions of 823 cm^{-1} is not apparent in the 1D FTIR [17] and, therefore, it is difficult to directly compare the conversion rate of cyanate group to that of maleimide by 1D FTIR spectra. Fortunately, generalized 2D correlation analysis, a recently developed technique, is able to offer a approach to observe the specific sequence of certain events taking place in the system and might provide information that is hard to be detected by conventional 1D analysis.

2D correlation analysis was introduced by Noda [30,31] and was originally intended to be used in conjunction with dynamic rheo-optical data. More recently, Noda [32] has further extended the underlying theory by introducing a more general formalism to include dynamic IR signals having any arbitrary waveform. This novel method can handle spectral fluctuations as an arbitrary function of time or any other physical variables and is able to probe the specific sequence of certain events taking place with the development of a controlling physical variable, which is of much significance in the dynamic analysis [33–36].

Figs. 8–10 are synchronous and asynchronous 2D FTIR correlation spectra (contour maps) of BC-0, BC-1 and BC-2 during isothermal curing at the temperature of 200 °C. The correlation peak (823, 2267) was identified in the synchronous 2D correlation spectrum, while the reaction sequence of cyanate group (823 cm^{-1}) and bismaleimide (2267 cm^{-1}) was determined by the asynchronous 2D correlation spectrum.

According to Noda [30], the sign of asynchronous correlation peak $\psi(v_1,v_2)$ gives information about the sequential order of intensity changes between band v_1 and band v_2. If the sign of the asynchronous intensity $\psi(v_1,v_2)$ is positive (unshaded area), band v_1 varies sooner compared with band v_2, while the negative asynchronous intensity (shaded area) implies the opposite phenomena on the condition that the sign of a synchronous intensity $\varphi(v_1,v_2)$ at the same coordinate is positive. For example, in Fig. 8 (BC-0), the positive asynchronous intensity $\psi(823, 2267)$ and the positive synchronous intensity $\varphi(823, 2267)$ revealed that the reaction of maleimide (823 cm^{-1}) occurred sooner than the reaction of the cyanate group (2267 cm^{-1}). While, Fig. 9 (BC-1) shows the contrary result: the negative intensity $\psi(823, 2267)$ and the positive intensity $\varphi(823, 2267)$ revealed that the reaction of cyanate group (2267 cm^{-1}) was sooner than that of maleimide (823 cm^{-1}), which meant the addition of NP accelerated the reaction speed of BADCy in the BC-1 relative to BC-0. However, BC-2 (Fig. 10) is significantly different from BC-0 and BC-1: there has no asynchronous correlation peak between cyanate group (2267 cm^{-1}) and maleimide (823 cm^{-1}) while the synchronous intensity $\varphi(2267, 823)$ is positive. According to the rule of Noda it means the reaction of cyanate group was synchronous with the reaction of bismaleimide.


(a) Synchronous Spectrum

(b) Asynchronous Spectrum

Fig. 8. 2D correlation spectrum of BC-0: (a) synchronous; (b) asynchronous.

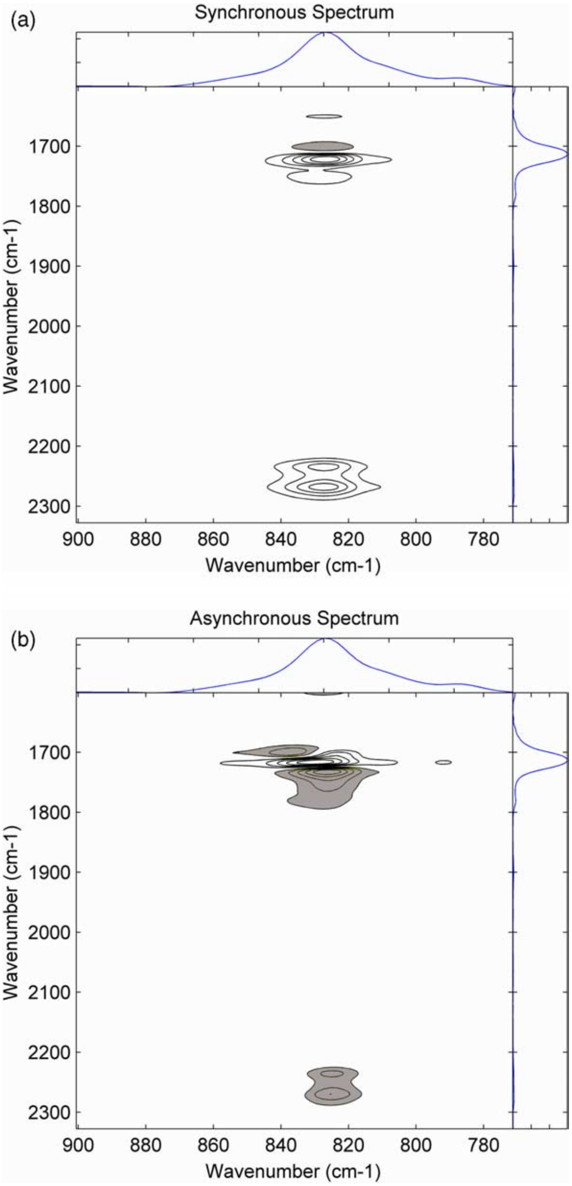


Fig. 9. 2D correlation spectrum of BC-1: (a) synchronous; (b) asynchronous.

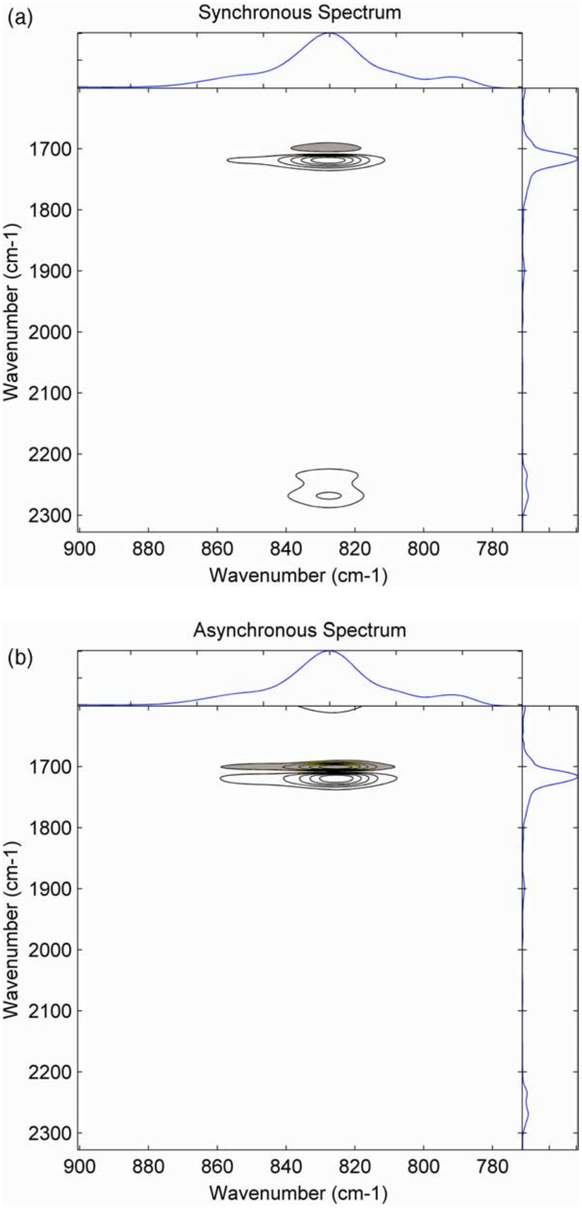


Fig. 10. 2D correlation spectrum of BC-2: (a) synchronous; (b) asynchronous.

From the asynchronous 2D FTIR correlation analysis, two remarkable conclusions could be drawn: (a) in both blends of BC-0 and BC-1 there existed the difference in the reaction sequence of BADCy and BMI: in the case of BC-0, BMI reacted faster than BADCy, while in the case of BC-1, BADCy reacted faster than BMI. (b) In BC-2, BADCy and BMI reacted simultaneously.

Therefore, combined with the results of FTIR, DSC and DMA, it revealed that BMI and BADCy in BC-0 and BC-1 cured independently and formed two kinds of network. In BC-2, it apparently illustrated the occurrence of co-reaction between BADCy and BMI.

Summary, the cure mechanism of the blends of dicyanate ester and bismaleimide was related to the catalyst presented in the blends. The cyanate curing catalyst, nonylphenol, results in the form of IPN, while the ring closure catalyst, *p*-toluene sulphonic acid, leads to the occurrence of co-reaction. Thus, if unpurified bismaleimide including the ring closure catalyst was regarded as non-catalyzed component, the inexact or at least incomplete conclusion may be deduced.

4. Conclusions

The results of the present work indicated that there existed two kinds of cure mechanism for the blends of dicyanate ester and bismaleimide: independently cure mechanism and co-reaction mechanism. Without catalyst, BADCy and BMI cured independently and formed two kinds of networks; the addition of NP promoted the cure of BADCy, but did not change the cure mechanism of two components. Moreover, the presence of PTSA resulted in co-reaction between dicyanate ester and bismaleimide 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.

References

[1] Meng JR, Hu X, Boey FYC, Li L. Polymer 2005;46:2766.
[2] HR, Hu X. Polymer 2004;45:9011.
[3] Liu YL, Chen YJ. Polymer 2004;45:1797.
[4] Jeng RJ, Chang CC, Chen CP, Chen CT, Su WC. Polymer 2003;44:143.
[5] Gaku M. US Patent 4110364; 1978.
[6] Christie, Frederick R. US Patent 4456712; 1984.
[7] Herner Jr, Robert E. US Patent 4731426; 1988.
[8] Penczek P, Kaminska W. Adv Polym Sci 1990;97:41.
[9] Nair CPR, Francis T, Vijayan TM, Krishnan K. J Appl Polym Sci 1999; 74:2737.
[10] Hamerton I. High Perform Polym 1996;8:83.
[11] Barton JM, Hamerton I, Jones JR. Polym Int 1992;29:145.
[12] Barton JM, Hamerton I, Jones JR. Polym Int 1993;31:95.
[13] Enoki T, Takeda T, Ishii K. Netsu Kokasei Jushi 1995;16(1):1.
[14] Nair CPR, Francis T. J Appl Polym Sci 1999;74:3365.
[15] Hong JL, Wang CK, Lin RH. J Appl Polym Sci 1994;53:105.
[16] Lin RH, Lee AC, Lu WH. J Appl Polym Sci 2004;94:345.
[17] Lin RH, Lu WH, Lin CW. Polymer 2004;45:4423.
[18] Kwiatkowski. US Patent 3839287; 1974.
[19] Renard. US Patent 3960887; 1976.
[20] Zahir. US Patent 4288583; 1981.
[21] Nishikawa. US Patent 4460783; 1984.
[22] Adams. US Patent 4464520; 1984.
[23] Butler. US Patent 4855450; 1986.
[24] Stockinger. US Patent 5070163; 1991.
[25] Amaguchi. US Patent 5206438; 1993.
[26] Yamaguchi. US Patent 5484948; 1996.
[27] Kissinger HE. Anal Chem 1957;29:1702.
[28] Brown IM, Sandreczki TC. Macromolecules 1990;23:94.
[29] Socrates G. Infrared characteristic group frequencies. New York: Wiley; 1980.
[30] Noda I. J Am Chem Soc 1989;111:8116.
[31] Noda I. Appl Spectrosc 1990;44:550.
[32] Noda I. Appl Spectrosc 1993;47:1329.
[33] Liu Y, Ozaki Y, Noda I. J Phys Chem A 1996;100:7326.
[34] Ozaki Y, Liu Y, Noda I. Macromolecules 1997;30:2391.
[35] Czarnecki MA, Maeda H, Ozaki Y, Suzuki M, Iwahashi M. J Phys Chem A 1998;102:9117.
[36] Ren Y, Shimoyama K, Ninomiya T, Matsukawa K, Inoue H, Noda I, et al. Appl Spectrosc 1999;53:919.