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Hygrothermal stability of dicyanate-novolac epoxy resin blends

Baochun Guo*, Demin Jia, Weiwen Fu, Qinghua Qiu

Department of Polymer Materials and Engineering, South China University of Technology, Guangzhou 510640, PR China

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Abstract

The chemical nature of the changes in a cyanate ester-novolac epoxy resin blend caused by hygrothermal ageing and the effects of the residue reaction in the blends on the hygrothermal ageing resistance were studied. The blends with epoxy molar fraction less than 0.5 absorb much less moisture in boiling water than does the homopolymer of the cyanate ester. The moisture uptake of the blend decreases with the extent of cure. The results from dynamic mechanical thermal analysis (DMTA) and Fourier transform infrared spectroscopy (FTIR) indicate that the blends possess superior hygrothermal stability compared to homopolycyanate. The results also indicate that the long-term hygrothermal ageing may cause substantial changes in the chemical nature of the blend when the cure extent is not sufficiently high.

Keywords: Cyanate ester; Novolac epoxy; Hygrothermal stability

1. Introduction

Cyanate ester resins, which have been commercialised since the late 1970s, are high performance thermosetting resins containing two or more cyanate ester functionalities. Due to their special structure and reactivity, the cured cyanate ester resins possess a number of attractive features, including strong hydrophobicity, high thermal stability, excellent dielectric properties, excellent adhesion to metals and processability comparable with epoxies etc. [1,2].

Despite the attractive properties, cyanate ester resins have also been modified with other polymers to improve their performance further or reduce cost. Actually the relatively high price is a big obstacle to the development of these resins. Blending with epoxy resins is one of the most important modifications and most commercial cyanate ester prepregs are made from cyanate ester/epoxy blends [3]. Cyanate ester/epoxy blends are not simple physical blends. A very complicated co-reaction occurs in the blends [4–9]. The process of insertion/isomerization/ring cleavage is a typical reaction mechanism [4,5]. Recently, a novel reaction during the curing of dicyanate-epoxy novolac resin blends was announced [9]. The cyanate ester-novolac epoxy resin blends possess a combination of high thermal stability, low electric loss and good processability and are suitable for application as the matrices of high performance composites [10,11].

It is well known that the presence of absorbed water may have a devastating effect on the thermomechanical properties of a resin and the fibre reinforced resin composites, especially in the case of epoxy resins [12]. So water uptake characteristics and T_g values are of great interest for high performance applications such as aircraft primary structures. As a consequence, a thorough knowledge of the possible effects on cyanate ester-novolac epoxy resin blends of hygrothermal ageing is crucial to the future use of these materials in these applications. The cure extent of a thermosetting resin is critical to the final properties including hygrothermal ageing resistance of the resin. To study the residue reaction on the hygrothermal ageing resistance, cyanate ester-novolac epoxy resin blends with different cure extent were prepared. This paper aims to determine the chemical nature of the changes in the cyanate ester-novolac epoxy resin blend caused by hygrothermal ageing and the effects of the residue reaction in the blends on the hygrothermal ageing resistance.

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* Corresponding author.
E-mail address: psbcguo@scut.edu.cn (B. Guo).

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Table 1
Curing cycles for preparing the blends with different cure extent

Sample code	Cure schedule
A	180 °C/1 h
B	180 °C/2 h
C	180 °C/1 h + 200 °C/1 h
D	180 °C/1 h + 220 °C/1 h
E	180 °C/1 h + 220 °C/2 h

2. Experimental

2.1. Materials

Bisphenol A dicyanate ester, with a degree of crystallinity (>99.5%) with the tradename AroCy B-10 was supplied by Ciba Specialty Chemicals.

Novolac epoxy resin with tradename F-44 was supplied by Shanghai Resin Plant. Its epoxy value was 0.47 mol epoxy group per 100 g resin.

2.2. Sample preparation

Blends with different epoxy molar fraction (defined as f_e) were melted together and degassed at 110–120 °C for 1 h. The degassed melt was poured into a Teflon coated mould which was heated to 180 °C. The blends were then cured at 180 °C for 1 h and postcured at 220 °C for 2 h. To prepare the blends with different cure extent, the blend with f_e of 1 was cured according to the schedules in Table 1. Before curing, the blend was also degassed at 110–120 °C for 1 h.

2.3. Methods and instrumentation

To determine the moisture uptake, the specimens were dried at 105 °C until a constant weight was obtained prior to immersion in boiling distilled water. Moisture uptake was recorded by weighing the sample after different times of exposure. The percentage gain at any time was determined by the following equation:

$$\text{Moisture uptake} = (W - W_0)/W_0 \times 100\%$$

where W_0 and W denote weight of dry material and weight of exposed material. DMTA was conducted on a TA DMA2980 instrument from TA Instruments. The dual cantilever mode was selected. The heating rate was set at 5 °C/min and the frequency at 5 Hz. The aged samples were stored at room temperature for 2 weeks and heated to 105 °C for 0.5 h before testing to eliminate the influence of moisture.

A Nicolet Magna 760 FTIR spectrometer at a resolution of 4 cm^{-1} in absorbance mode was employed for structural studies. Finely powdered cured resin was ground with KBr powder and pressed into a pellet for FTIR testing.

The TA Modulated DSC 2910 was employed to evaluate the cure extent of the partially cured blends. Circa 5 mg of resin was sealed in an aluminium pan, which could resist a pressure up to 10 MPa. Nitrogen with a flow rate of 40 ml/min was used as purge gas.

3. Results and discussion

3.1. Effects of blending proportion and cure extent on the moisture uptake

Fig. 1 shows the moisture uptake profile of polycyanate and its blends with novolac epoxy resin. It can be seen from the figure that only the sample with f_e of

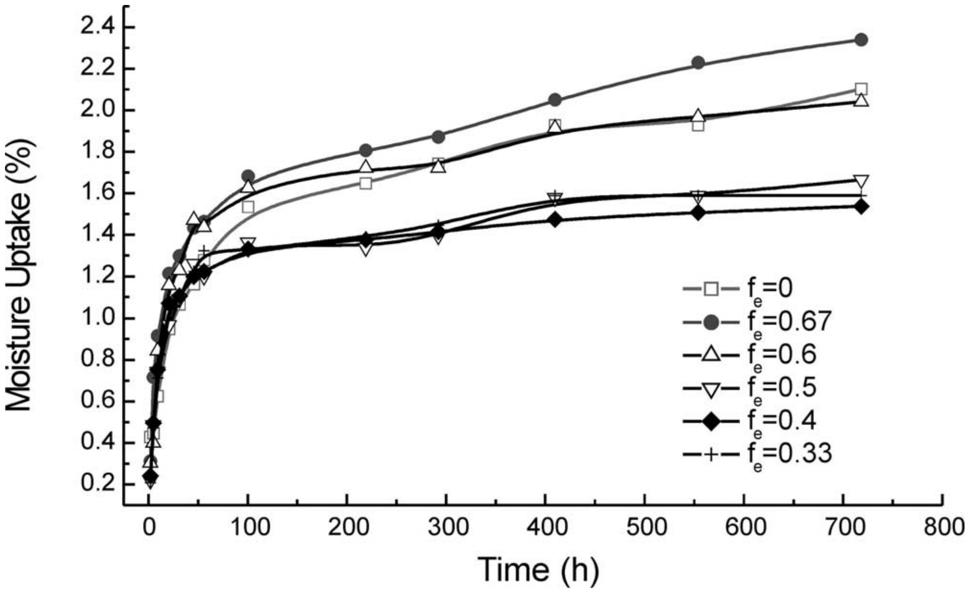


Fig. 1. Moisture uptake profile of the blends with different f_e value.

0.67 absorbed more moisture than the homopolycyanate. The blends with f_e value below 0.5 take up much less moisture and reach their saturation stage more easily. The saturated moisture uptake of the blends with f_e value below 0.5 are all about 1.6%, which is much smaller than that of the homopolymer, i.e. 2.5% [13]. It is therefore indicated that the blends with f_e lower than 0.5 are more hydrophobic than the homopolymer. That blends with higher polarity are more hydrophobic than the homopolymer is probably because the free volume of the blends is smaller than that of the homopolymer. The homopolymer occupies relatively larger free volume since it contains a number of the intramolecular triazine bicyclophane cage structures.

The apparent conversions for the partially cured samples A, B, C, D and E, evaluated from the MDSC data, are 80.2, 90.2, 92.5, 96.7 and 97.6% respectively. The moisture uptake profile of the blends (f_e is 0.5) with different extent of cure is shown in Fig. 2. It is shown that the moisture uptake decreases with the extent of cure. It is different from the moisture uptake regularity of the homopolycyanurate. The moisture uptake of polycyanurate increases with its extent of cure as the polarity decrease with its extent of cure and the free volume increases with the extent of cure, which may be due to the increasing fraction of the intramolecular product [14]. The structure of the cyanate-epoxy blends, however, is substantially different from that of the polycyanate. The blends possess more polar groups and have different free volume characteristics. During the long-term hygrothermal ageing, the unreacted cyanate group trapped in the network may react with the water. There may be two reasons for the moisture uptake regularity of the blends. One is the presence of the residual group reactive towards water. The other may be the changed free volume characteristics compared to that of homopolycyanate. The changes in free volume may be due to the combination of kinetics of glass transition and/or structural developments [15].

3.2. *Effects of the hygrothermal ageing on the thermomechanical properties of the blends*

To reveal the effects of the hygrothermal ageing on the T_g and sub-T_g transitions, DMTA was performed before and after ageing and the spectra are shown in Fig. 3. The characteristics of these curves are tabulated in Table 2. The α transition corresponds to the primary transitions of the blends. Comparable to the results of Mathew [16], a single T_g is observed in these DMTA curves, which indicates that the polycyanurate is compatible with the oxazolidinone. The T_g of the blend decreases with f_e since the fraction of the stiffer polycyanurate decreases with f_e. The T_g results show that the T_g does not vary significantly when f_e is lower than 0.5 while decreases rapidly when f_e is higher than 0.5. The β relaxation is observed around −60 °C. The temperature of the β relaxation increases slightly with f_e. The β relaxation of novolac epoxy-aromatic amine networks is almost at the same temperature [17]. The above β transition may be due to the relaxation of polyether segments in novolac epoxy resin.

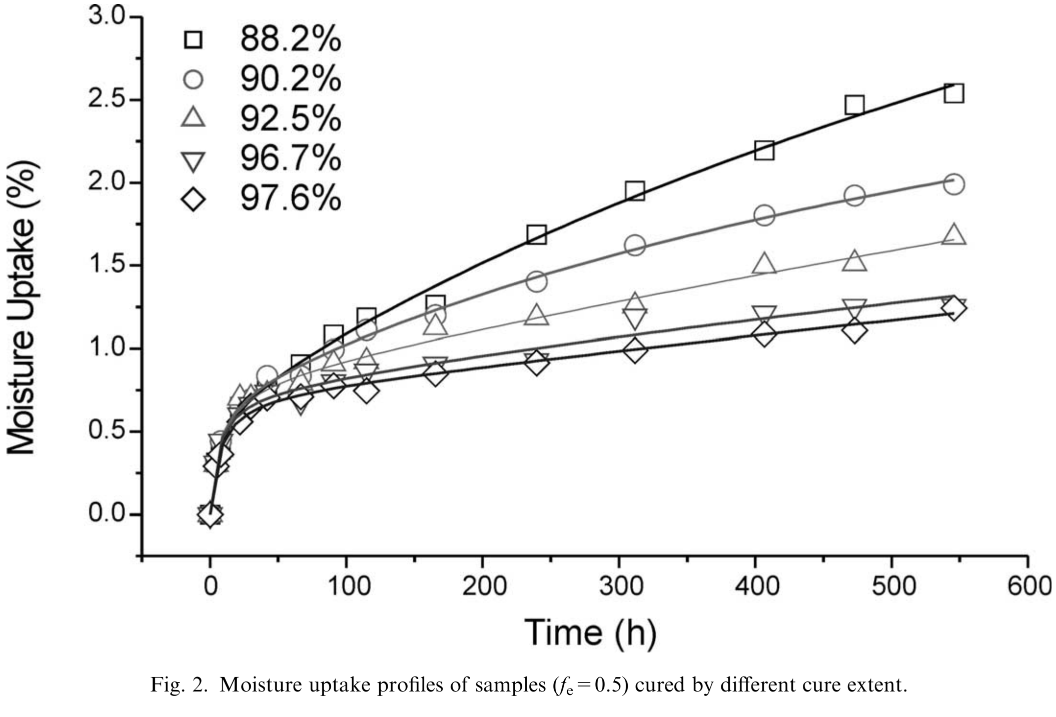


Fig. 2. Moisture uptake profiles of samples ($f_e = 0.5$) cured by different cure extent.

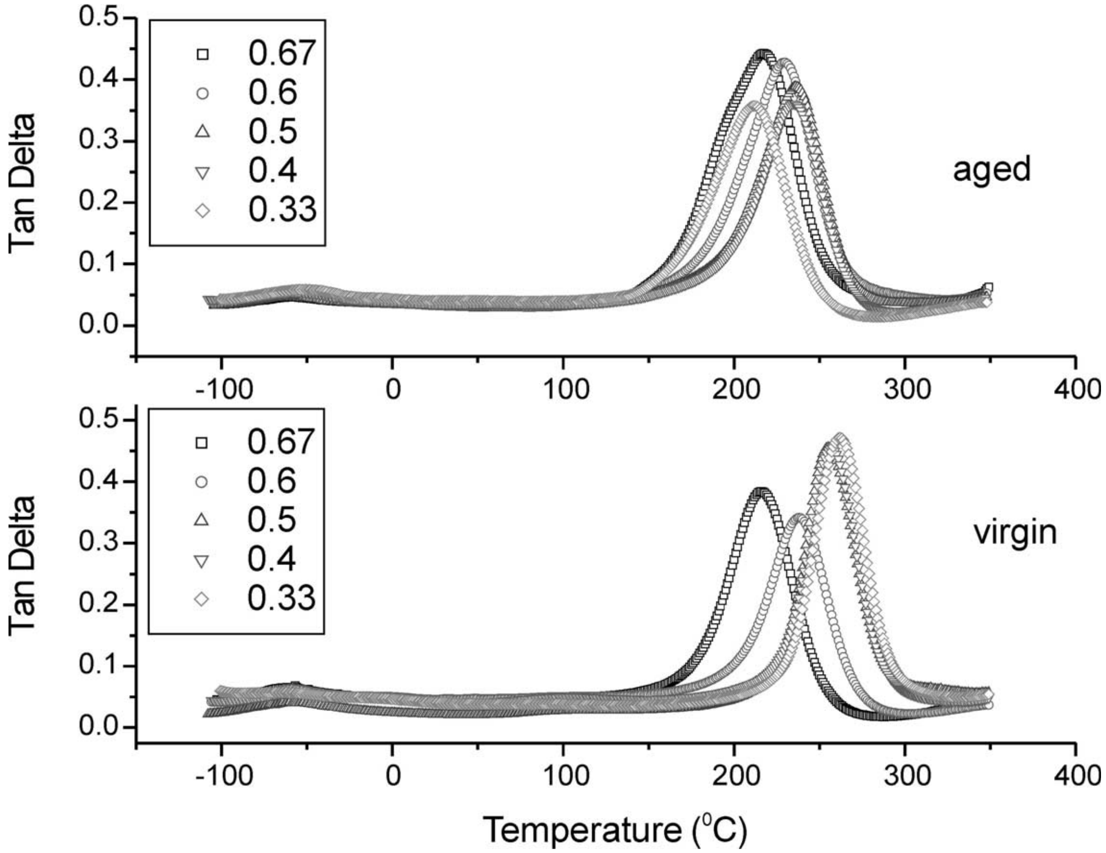


Fig. 3. Effects of hygrothermal ageing on the DMA spectra of the blends.

Table 2
Relaxation peak temperatures before and after hygrothermal ageing (all temperatures are in °C)

f_e		0.67	0.6	0.5	0.4	0.33
Virgin	α	216	238	255	257	262
	β	−57	−59	−60	−59	−65
Aged	α	217	229	236	235	212
	β	−59	−59	−55	−56	−51

After hygrothermal ageing, the T_g of the sample still decrease with f_e with an exception of the blend with f_e of 0.33, in which the T_g decreases substantially. The decreases of the samples with f_e of 0.33 to 0.6 after ageing are 50, 22, 19 and 9 °C respectively. The T_g of the sample with f_e of 0.67 basically remains unchanged. The results show that extent of the decrease in T_g decreases with f_e. The decrease in T_g reveals the effects of hygrothermal ageing on the chemical and physical structures of the networks since samples were dried before DMTA measurements. Despite the relative low moisture uptake, long-term hygrothermal ageing could affect the molecular structure of the polycyanurate and its blends with epoxy. The blends are more resistant to water than the homopolycyanate since the oxazolidinone is more hydrophobic than cyanurate, which will be substantiated further by the following FTIR results. The temperature of β relaxation decreases slightly with f_e. The reason for the change is still being investigated.

3.3. *Effects of hygrothermal ageing on the structures of the blends*

To substantiate the above DMTA results, FTIR experiments were performed before and after hygrothermal ageing. Fig. 4 shows a relative strong absorption at 1718 cm^{-1} in the FTIR spectrum of the aged polycyanate sample, which was probably due to the cyanic acid species. It is reported that the formation of cyanic acid is the first step of the decomposition of polycyanurate [18,19]. Fig. 5 shows that the FTIR spectrum of the blend with f_e of 0.67 was basically unchanged after the hygrothermal ageing. These results demonstrate that the oxazolidinone-containing blends are more hydrophobic and more resistant to hygrothermal ageing compared to the polycyanurate. The hydrolysis is illustrated in the Scheme 1 [18,19].

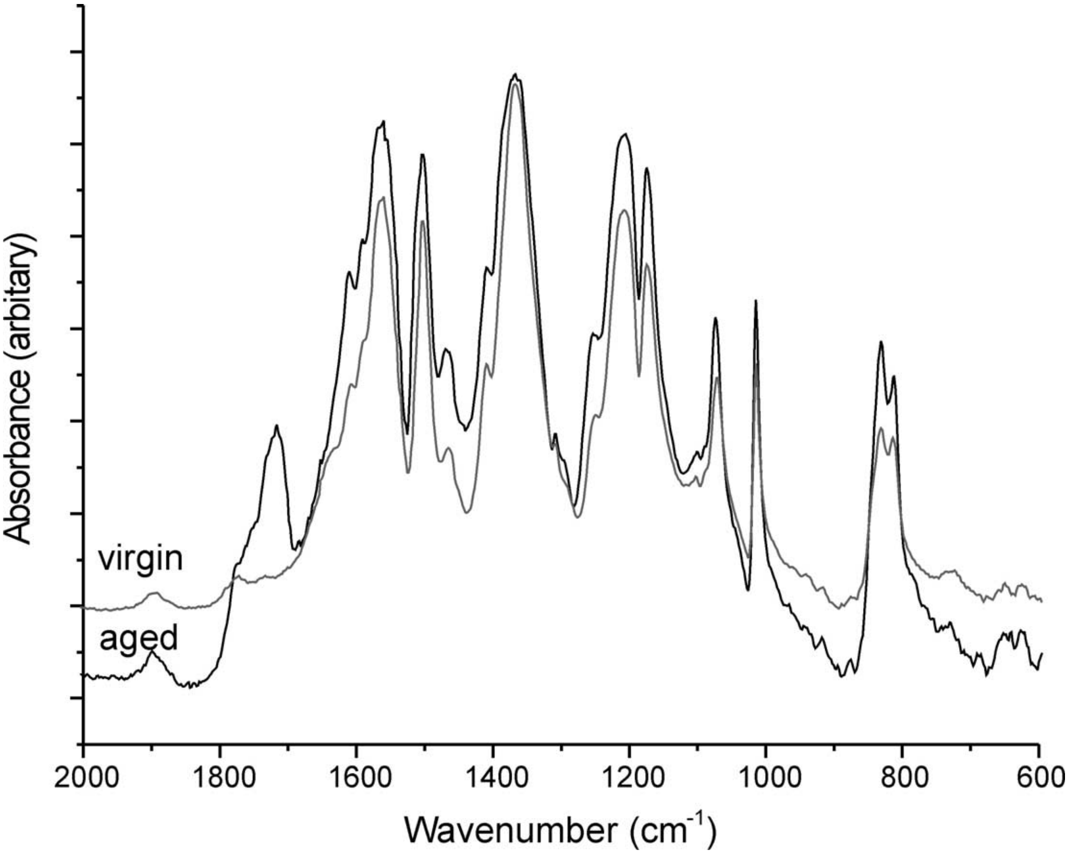


Fig. 4. FTIR spectra of virgin and aged polycyanate samples.

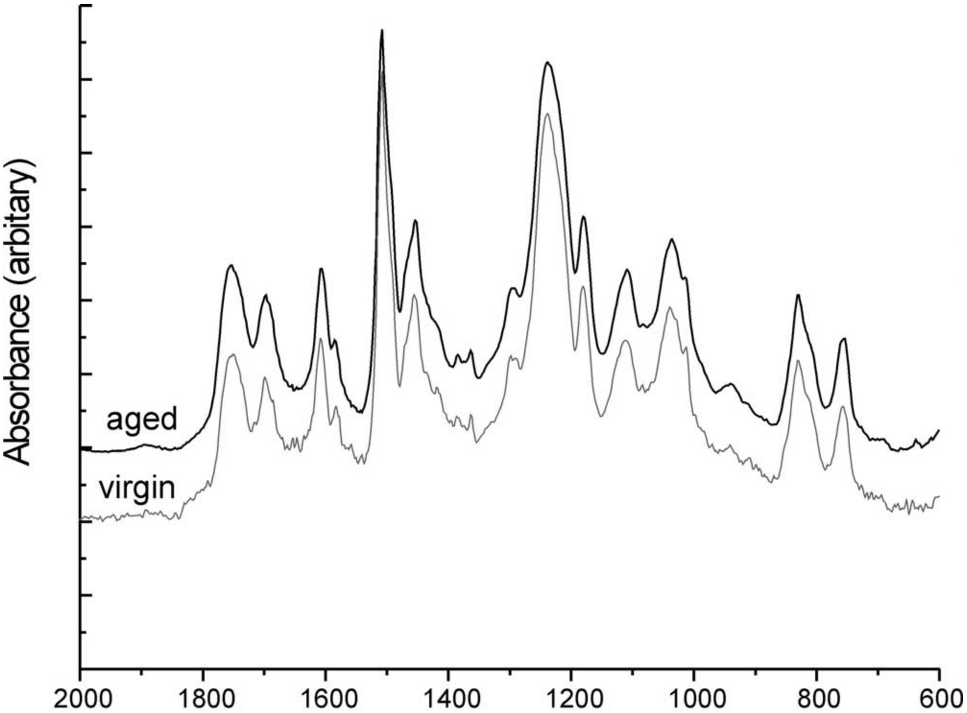


Fig. 5. FTIR spectra of virgin and aged blend with f_e of 0.67.

Figs. 6–8 show the FTIR spectra of the blends with different cure extent. It is shown that the hygrothermal ageing has less effect on the structure in the blend with higher cure extent. When the cure extent is relatively high (97.6%), the hygrothermal ageing has minimal effect on its structure. When the cure extent is lower than this level, structural changes are observed. The relative absorbance of isocyanurate (1695 cm^{-1}) increases after the hygrothermal ageing. When the cure extent is lower than 90%, significant structure changes were

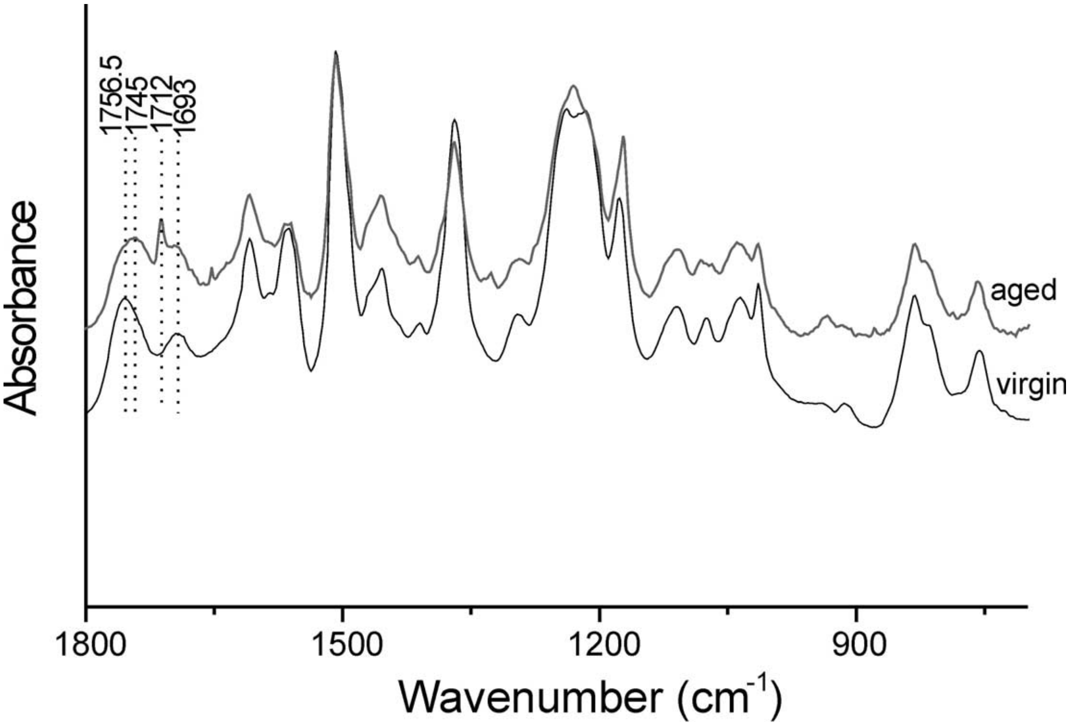


Fig. 6. Effect of hygrothermal ageing on the structure of the sample A.

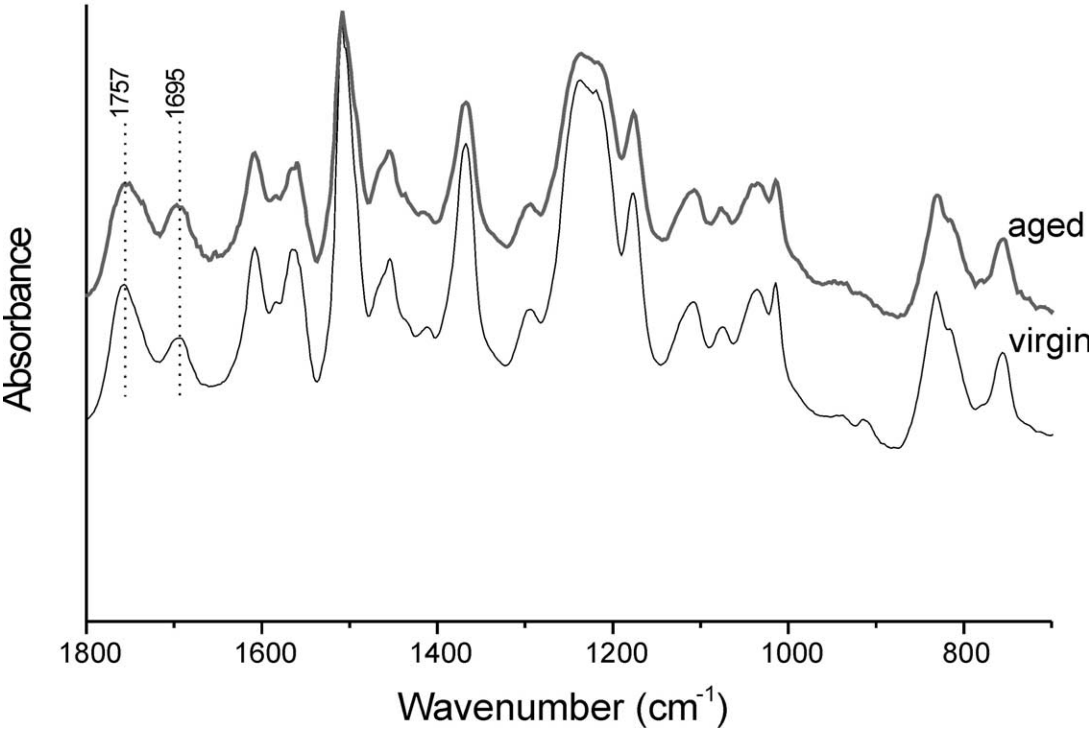


Fig. 7. Effect of hygrothermal ageing on the structure of the sample B.

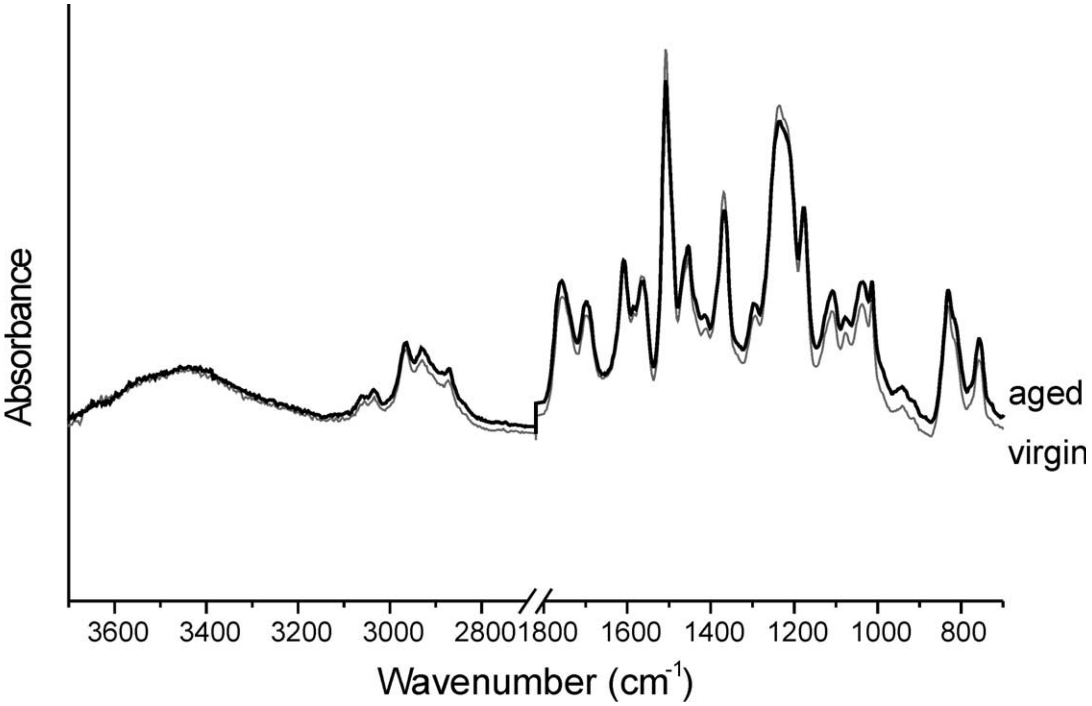
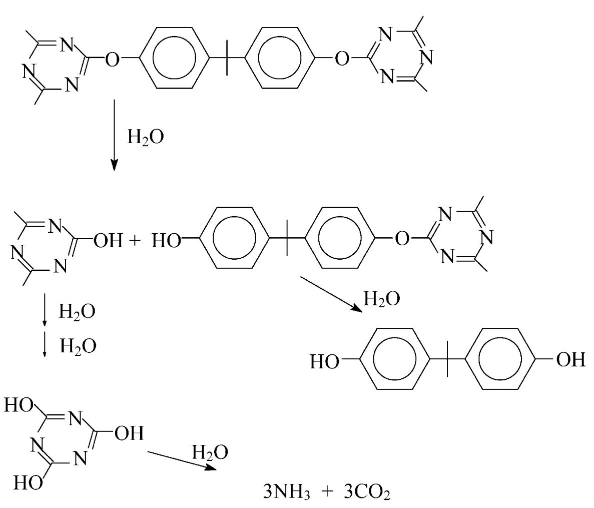


Fig. 8. Effect of hygrothermal ageing on the structure of the sample D.



Scheme 1.

observed. Not only the absorbance at 1693 cm^{-1} increases, but also a relatively strong peak at 1712 cm^{-1} is observed. This new peak should not be due to carbamate, the product from cyanate group and water, since the cyanate groups disappear at such a cure extent [9]. The long-term hygrothermal ageing, however, may cause the hydrolysis of cyanurate especially when the network is relatively loose. Therefore the peak at 1712 cm^{-1} may also be due to cyanuric acid, the hydrolysis product of cyanurate.

4. Conclusions

The moisture uptake of dicyanate-epoxy novolac resin blends with f_e lower than 0.5 is substantially lower than that of the homopolycyanate. The saturated moisture uptake of those blends is around 1.6%. The moisture uptake of the blend decreases with the cure extent.

The DMTA results showed a single glass transition of the dicyanate-epoxy novolac resin blends before and after hygrothermal ageing. The T_g decreases with f_e before and after hygrothermal ageing. The extent of decrease in the T_g decreases with f_e.

The DMTA and FTIR demonstrate the superior hygrothermal resistance of the dicyanate-epoxy novolac resin blends compared to the homopolycyanate. Long term hygrothermal ageing could has significant effects on the structure of the blend when the cure extent is not sufficiently high, for example, less than 90%.

Acknowledgements

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