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Study on the Novel Dicyanate Ester Resin Containing Naphthalene Unit

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Abstract: The novel dicyanate ester resin containing naphthalene unit (DNCY) was synthesized, and characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis (EA). The thermal properties of DNCY resin was studied by thermal degradation analysis at a heating rate of 10 °C /min^{-1} in N_2 and air. The DNCY resin exhibited better thermal and thermal-oxidative stability than bisphenol A dicyanate (BACY) resin.

Keywords: Naphthalene unit, dicyanate ester resin, synthesis, thermal properties.

Many thermoplastic polymers containing naphthalene structure such as polyimide[1], PEEK[2], and PEN[3, 4] are known to have excellent thermal stability and used for high-quality fibers, magnetic recording tape, flexible printed circuits, *etc*. However, high molecular weight condensation-type polyimides usually suffer from processing problems due to their insolubility, infusibility, and the volatiles evolved during the ring formation. Thermal setting resins containing naphthalene have been reported such as epoxy, acetylene-terminated resins[5], *etc*. but their limitation on the upper use temperature and poor hot /wet performance restrict their application. Cyanate ester resins have attracted increasing attention due to their highly desirable chemical, electrical, and mechanical properties for several applications[6~8], and have been evaluated as potential replacement for epoxy resins. In recent years, some cyanate ester resins containing naphthalene ring, such as 2,6-dihydroxynaphthalene dicyanate, 1,5-dihydroxynaphthalene dicyanate and (2, 3-dihydroxy)1, 1-dinaphthalene dicyanate, have been synthesized. But their applications were limited due to the bad processability of monomers. Few concern the cyanate ester resin containing 2,7-dihydroxynaphthalene structure (DNCY).

The cyanate ester containing naphthalene, 2,7-dihydroxynaphthalene dicyanate (DNCY), was synthesized by two steps as shown in **Scheme 1**[9,10]. The potassium cyanide was reacted with bromine in H_2O to give cyanogen bromide. The 2,7-dihydroxynaphthalene was reacted with cyanogen bromide in acetone in the presence of triethylamine at the temperature from -5 to 10 °C to give 2,7-dihydroxynaphthalene dicyanate (DNCY). The yield of DNCY was 83.2%. m.p.: 138~139 °C. Elemental ana-

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Scheme 1 Synthesis of 2,7-dihydroxynaphthalene dicyanate (DNCY)

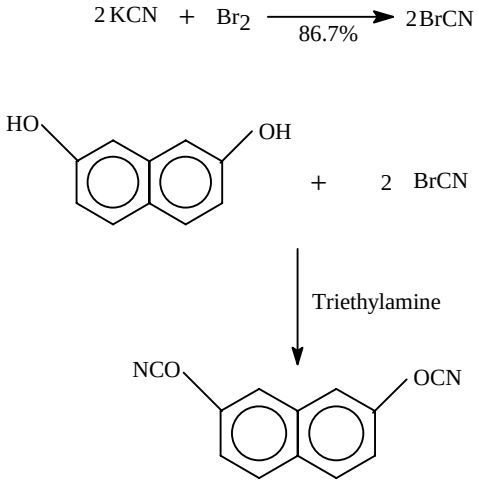


Figure 1 TGA thermograms of different dicyanate esters resin systems in N_2 at a heating rate of 10°C min^{-1}

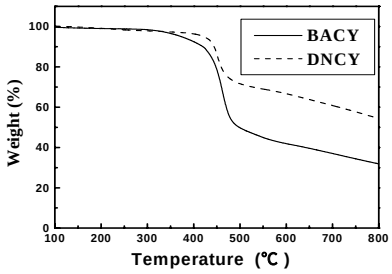
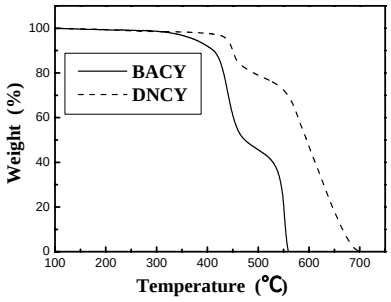


Figure 2 TGA thermograms of different dichanate ester resins systems in air at a heating rate of 10°C min^{-1}



lysis calculated for $C_{12}H_6N_2O_2$: (%) C 68.57, H 2.86, N 13.33; Found C 68.49, H 2.89, N 13.53%. The monomer of DNCY was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR, which proved that the monomer had been synthesized successfully.

Thermal stability of the cured DNCY resin was shown in **Figure 1** (thermal stability) and **Figure 2** (thermal-oxidative stability). The result of the cured BACY resin is also depicted as a comparison in respective graphs. Obviously, as shown in **Figure 1** and **Figure 2**, the thermal stability of dicyanate ester resin has been enhanced due to the introduction of the naphthalene in structure resin networks, especially the anaerobic char yields of DNCY has been raised more 20% at 700°C than that of BACY. The T_i of BACY resin in air were lower than that in N_2, while that of DNCY in N_2 were nearly the same as it was in air，and especially the second thermal degradation rate was obviously decreased due to the effect of naphthalene in network structure. It illustrated that naphthalene ring played a more important role towards the thermal-oxidative stability than the thermal stability. Further research on the DNCY resin is in progress in our laboratory.

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