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Viscoelastic, Thermal and Mechanical Properties of Dicyclopentadiene Bisphenol Diyanate Ester / Epoxy Co-polymers

Jieliang Wang, Guozheng Liang, Wen Zhao, Zengping Zhang

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University,
Xi'an Shaanxi 710072, China

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Abstract

Dicyanate ester containing dicyclopentadiene cycles and epoxy co-polymers were prepared by copolymerization between epoxy and dicyclopentadiene bisphenol cyanate esters (DCPDCE). Viscoelastic properties of the co-polymers were characterized by the technique of dynamic mechanical analysis (DMA), which indicated that the introduction of E51 in the co-polymers would effectively improve the toughness of DCPDCE, while the thermal dimensional stability would be weakened. Results from thermogravimetric analysis (TGA) are in good accordance with the T_g values from DMA curves. Mechanical testing of the cured co-polymers shows that E51 can improve the mechanical properties of the co-polymers while its usage is controlled among 5% to 15%.

Keywords

Viscoelastic, dicyclopentadiene bisphenol dicyanate ester, epoxy, co-polymers

Introductions

Cyanate ester resins have received much attentions in the areas of aerospace structure, aircrafts, dielectrics, some other government issues and civil industry products in recent years, because they have the high performance of mechanical properties, low water up-takes, good thermal and high temperature performance, perfect dielectric properties and low out-gassing during curing and so on. However, like most other thermosets, they have suffered the drawback of brittleness. Bisphenol A dicyanate ester (BADCy) was well studied on its curing and toughening. [1-10] Some methods are applied in improving the properties of BADCy such as polymer blending, co-polymerization, filler filling and fiber reinforcing. [11-14] Comparing to BADCy, dicyclopendiene bisphenol dicyanate esters (DCPDCE) have the advantages of higher glass transformation temperature, better dielectric properties, better thermal stability, lower water up-takes and more balanced mechanical properties.[15-16]

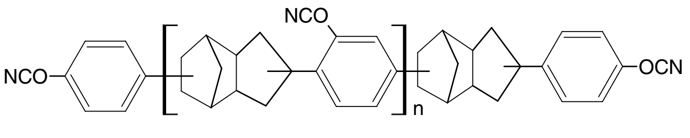
On the other hand, epoxies are widely used in adhesives and composites, and the co-polymerization between epoxy and BADCy are well studied by several groups since the appearances of cyanate esters.[17-19] Unfortunately, little work has been reported on the studies of DCPDCE.

In this work, co-polymers based on DCPDCE/E51 were fabricated. Viscoelastic, thermal and mechanical properties of the cured resin were studied via dynamic mechanical analysis, thermogravimetric analysis and mechanical testing, respectively.

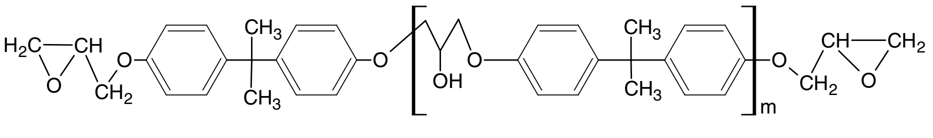
Experimental

Materials

DGEBA E51 was supplied by Yueyang Resin Company Limited (Hunan, China), its epoxy equivalent weight is 196. Dicyclopentadiene bisphenol cyanate ester (75% solution of MEK) was purchased from Shangyu Shengda Biochemical Co., Ltd (Zhejiang, China), and the solvent MEK was wiped off by distillation before its co-polymerization with epoxy. Chemical structures of them were shown in Figure 1. Other reagents are all used as received without any further treatment.



Dicyclopentadiene bisphenol cyanate ester DCPDCE



Epoxy E51

Figure 1 Chemical structures of DCPDCE and epoxy E51 (*n*=0~3, *m*=1~3)

Sample preparation

Epoxy E51 was dissolved in DCPDCE at 140°C without solvents, and the resultant clear mixture was degassed in a vacuum for 25min at 140°C. Then the mixture was poured into a mold, preheated at 150 ^{o}C, to obtain a plaque. The mold consisted of one pair of upright stainless plates spaced by a U-shaped silicon rubber stick (8 mm). The amount (mass fraction) of E51 was calculated on the basis of the matrix resin. The curing cycle was set on: 160^{o}C/2h+190^{o}C/2h +220^{o}C/2h+240^{o}C/5h. Then, the oven temperature was decreased from 240°C to room temperature at a cooling rate of 50°C/h.

Measurements

Dynamic mechanical analysis was performed on a DMA Q800 instrument (TA Instrument Company, USA) at a frequency of 3Hz.

Thermal stability of cured resins was obtained with a Perkin-Elmer thermogravimetric analyzer (TGA) with a heating rate of 10 °C/min in a nitrogen atmosphere.

The flexural strength was tested according to GB2570-1981 Standard of China and impact strength was tested according to GB2571-1981 Standard of China.

Results and Discussion

Viscoelastic properties of the cured co-polymers---------DMA analysis

Reactions between epoxy and dicyanate esters were well discussed in literatures. [8,20,21] Reaction between epoxy E51 and DCPDCE may be defined as Figure 2.

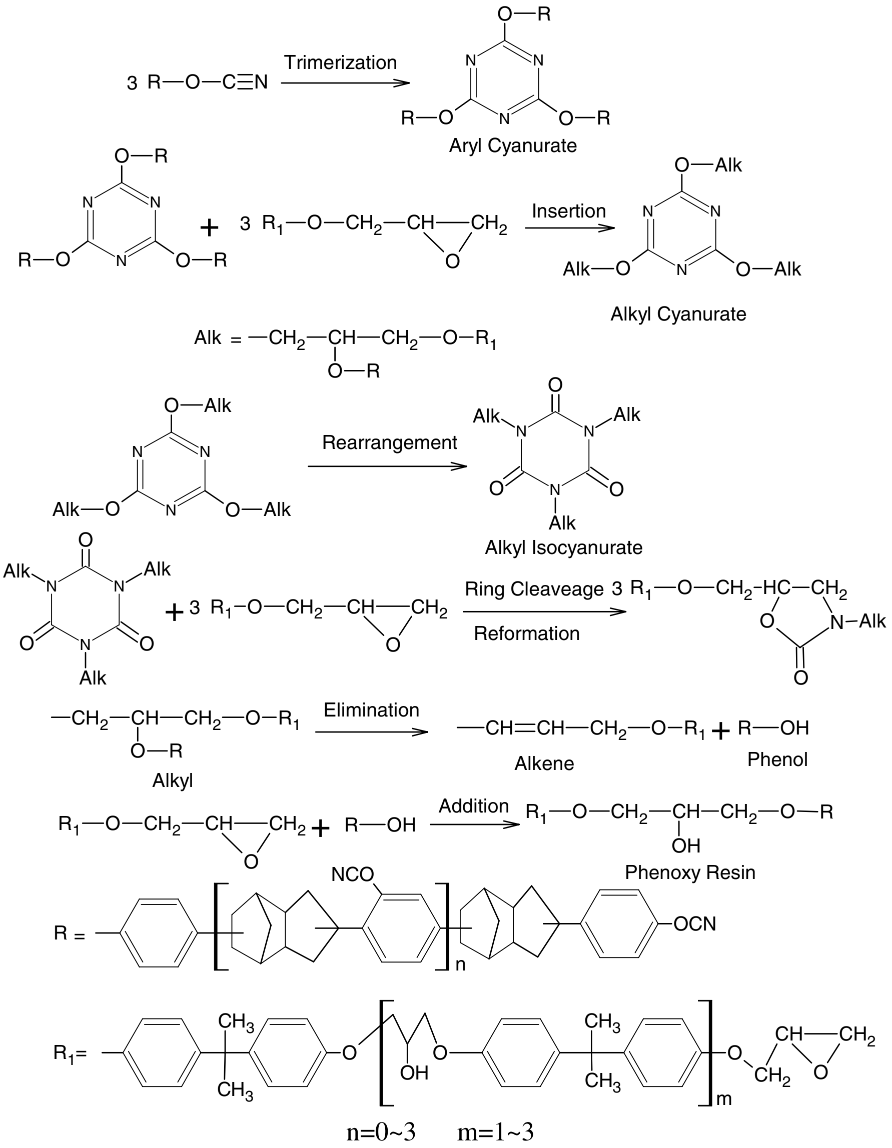


Figure 2 Reactions in the co-polymerize system based on DCPDCE and epoxy E51

DMA curves of original DCPDCE resin and the E51/DCPDCE 5/95, 15/85, 30/70 and 50/50 co-polymers are showed in Figure 3 and Figure 4. Figure 3 clearly showing that

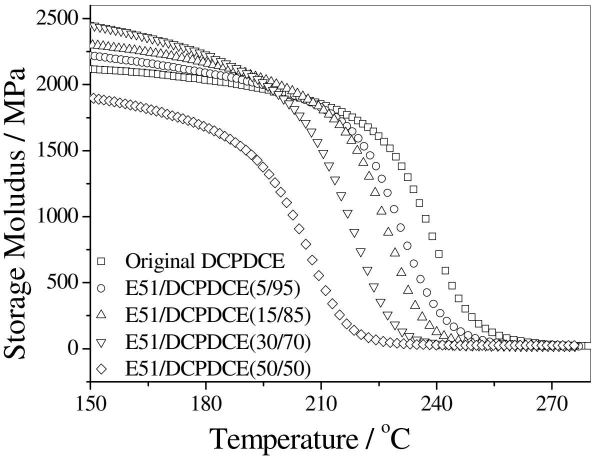


Figure 3 Storage modulus of cured DCPDCE/E51 co-polymers

the moduli of the cured co-polymers are higher than the neat DCPDCE resin when the content of E51 was lower than 30%(mass fraction) and $T<T_g$. It can be seen that when $T<T_g$, with the increasing of E51 used in the co-polymers, the storage modulus of the cured resin shows a trend of increasing in the beginning and then decreasing rapidly. While at $T>T_g$, the storage moduli of the co-polymers are lower than the neat dicyanate ester resin, and they decrease with an increase of E51 content. Thus neat dicyanate ester resin has higher dimensional thermal stability than the co-polymers, and at the same time the cured co-polymers are much tougher than the neat dicyanate ester resin. Reasons maybe lie in that the reaction between epoxy and cyanate groups would decrease the cross-linking density of the cured resin. Figure 4 shows that co-polymer E51/DCPDCE (5/95) has much higher intensity *tanδ* peak values than that of the neat DCPDCE and other E51/DCPDCE co-polymers. Glass transition temperature of neat DCPDCE and E51/DCPDCE co-polymers can be obtained from Figure 4, which indicates that the introduction of E51 would lower the T_g values of DCPDCE.

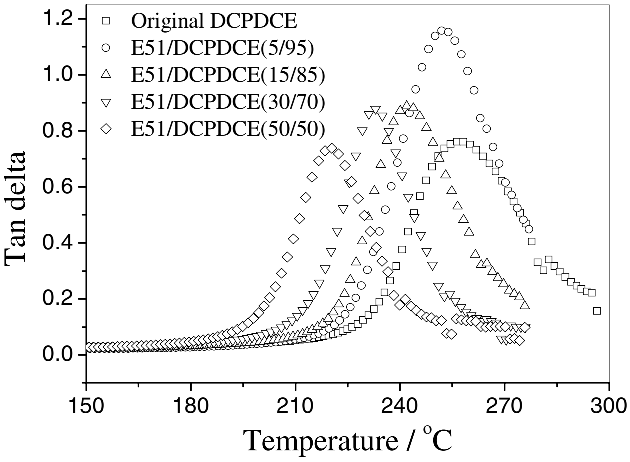


Figure 4 *Tanδ* values vs temperature of cured DCPDCE/E51 co-polymers

The more the epoxy used, the lower the T_g value of the co-polymer is. Reasons of the above phenomena are the co-polymerization reaction between DCPDCE and Epoxy, which is taking place in the system. The poor thermal properties of epoxy lowered the thermal stability of the co-polymers based on DCPDCE and epoxy.

Thermal stability of the cured co-polymers---------TGA analysis

Thermal stability of E51/DCPDCE co-polymers were characterized by TGA method and the results were shown in Figure 5. Weight loss data and the maximum degradation temperature of the cured resins were showed in Table 1. It indicates that the introduction of E51 would weak the thermal stability of DCPDCE resin. The more E51 used, the lower the initial decomposition temperature (T_i) and the maximum degradation temperature are. This is in good accordance with the results from *Tanδ* curves. In case of E51/DCPDCE (15/85), the T_i is 404.5°C, which is almost 30°C lower than that of the neat DCPDCE resin (434.0°C). Reasons lie in the reaction represented in Figure 6. Traizine ring in the cured DCPDCE resin would react with epoxy group, which will transform into oxazoline rings and oxazolidinone rings, and the thermal stability of these rings are much lower than that of traizine ring. What is interesting in the table is that E51/DCPDCE (50/50) has a higher T_i than E51/DCPDCE (30/70). This may come from the reaction balance in the systems.

Table 1 TGA data of the E51/DCPDCE co-polymers

Systems	Temperature on weight loss 5%/ °C	Maximum degradation temperature/ °C
Neat DCPDCE resin	434.0	449.4
E51/DCPDCE(5/95)	424.5	439.1
E51/DCPDCE(15/85)	404.5	436.8
E51/DCPDCE(30/70)	375.0	429.0
E51/DCPDCE(50/50)	380.4	414.4

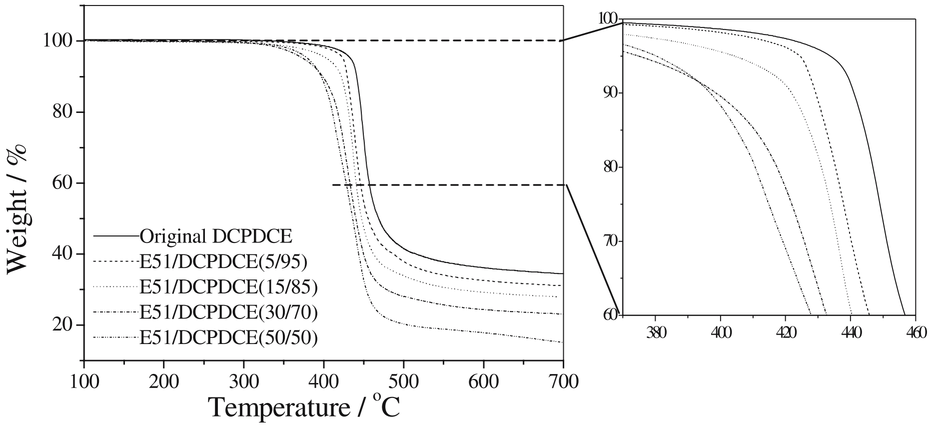


Figure 5 TGA curves of the cured co-polymers

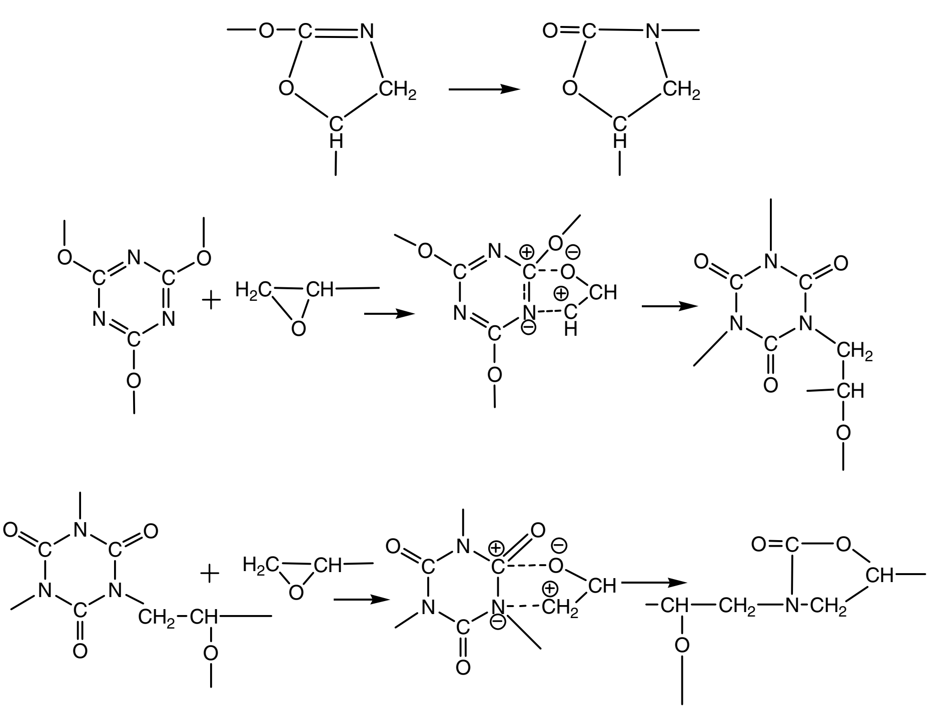


Figure 6 The transformation of oxazoline rings into oxazolidinone and the formation of oxazolidinone

Mechanical properties of the cured co-polymers

Cyanate esters suffered the drawbacks of brittleness, which limits their applications. The introduction of epoxy can always improve their toughness effectively. Mechanical properties of the cured co-polymers were represented in Figure 7. With

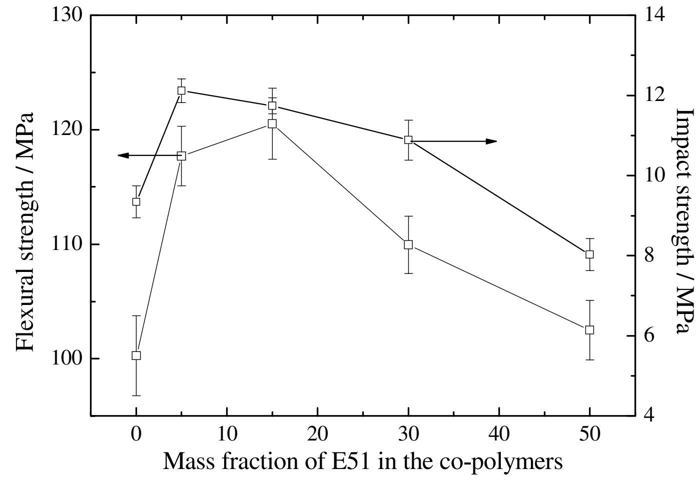


Figure 7 Mechanical properties of the cured co-polymers

the increasing of E51 content, the flexural strength expresses a trend of increasing in the beginning and then decreasing, it reaches the maximum value when 15% E51 was added, at this point, the flexural strength increases from 100.3MPa to 120.5MPa. Moreover, the impact strength of the co-polymers presents an trend same as the flexural strength, while it reach its maximum value when 5% E51 was used in the co-polymers. Low loading of epoxy would make up the possible defects of DCPDCE resin. But the oxazoline rings and oxazolidinone rings have lower mechanical properties than traizine rings, and these results in the decreasing of flexural and impact strength of the co-polymers. Take the flexural strength and impact strength of the cured co-polymers as a whole into account, the best E51 content in the co-polymers should be carefully controlled among 5% to 15%.

Conclusion

The introduction of E51 in the system with DCPDCE would increase the mechanical properties effectively. The toughness of the co-polymers was improved with the introduction of E51, which was clearly showed in DMA curves. But the addition of E51 would decrease the thermal stability and thermal dimensional stability of DCPDCE. Additionally, E51 can effectively improve the mechanical properties of DCPDCE resin.

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