# Study on Toughening Bismaleimide Resin with Active Liquid CTBN

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**ABSTRACT** Based on 4,4'-(bismaleimide)-diphenyl methane/o,o'-dially bisphenol A, the modification of the bismaleimide (BMI) resins with carboxyl-terminated butadiene-acrylonitrile (CTBN) rubbers was studied. The optimized resin has good comprehensive properties.

The effect of the amount of and the composition (acrylonitrile content) of the added CTBN on the properties of matrix system was studied. The results show that with the liquid CTBN of proper composition, the toughness of the BMI resins can be improved a lot, while the heat-resistance and other mechanical properties of the resins will not be decreased obviously.

**KEYWORD:** CTBN, Bismaleimide, Toughness

## INTRODUCTION

With excellent physical property retention at high temperature and in wet environments, almost constant electrical properties over a wide range of temperatures and low flammability properties, polyimides, especially thermosetting polyimides, are becoming more important in the aerospace and electric/electronic fields.

Being one of the two families of curable polyimide with industrial maturity, bismaleimides(BMIs) have developed to combine the good processibility of epoxy with the excellent heat tolerance of polyimides.The most commonly used monomer is BMDPM, which has a high melting point(161~163℃), when homopolymerized, highly brittle networks are usually formed. In order to be used in high performance fields, BMDPM must be modified to improve its fracture toughness without significant loss of its heat-resistant property.

Addition of a rubbery particle phase to a glassy polymer often enhances fracture toughness without significantly compromising the other desirable engineering properties. This approach was first introduced in early 1960s to overcome the inherent brittle of some thermoplastic polymers and was later employed for toughening of epoxy resins. There are many papers on rubber-modified epoxy resins, while only a few ones on the modification of bismaleimide resins with rubbers have reported.

St.Clair has reported an increase in the adhesive fracture energy of nadic-terminated polyimides, LARC-13, by the addition of amine-terminated silicone rubbers , whereas Varma et al. Have reported an increase in short beam shear strength of bismaleimide resins by the addition of amine-terminated rubbers. Shaw and Kinloch observed a significant increase in the fracture energy of bismaleimide resins by the modification with a CTBN rubber.

In this paper, we report on the modification of BMDPM/DABPA/active diluent/epoxy system with CTBN. The effect of the amount of and the composition (acrylonitrile content) of the added CTBN on the properties of this system was studied.

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## EXPERIMENTAL

**Preparation of Resins** The resin was synthesized by introducing CTBN, active diluent and epoxy step by step to BMDPM/DABPA system at 110~130℃ owing to their different reactivity.

**Preparation of Casted Resin Articles** The resin was poured into open casting molds and cured by the following schedule:2hours/110 ℃ (vacuum)+ 2hours/130 ℃ +2hours/150 ℃ +2hours/170℃+2hours/195℃.After these articles were picked out from the mold at room temperature, the post curing at 220℃ for 4 hours followed.

**Preparation of Resin Composite Reinforced by T-300 Carbon Cloth** After the cloth soaked with the resin solution with the solvent acetone was heated at 100~120℃ for about 3 hours, the pre-pregs were obtained. The laminate was produced under the pressure 190kgf/cm$^2$ at 195℃, with the following post curing at 220℃ for 4 hours.

**Testing of Properties** Gelation time was investigated by the method of little knife with about 1 gram resin. According to GB2918-82, the density of the cured resin was determined by the soaking method. DSC analysis was accomplished by a Dupont 2100 Differential Scanning calorimeter, with the sample being heated from 25~450℃ at 5℃/min under $N_2$. TMA and TGA were conducted with a Dupont 2100 thermomechanical Analyzer and a Dupont 2100 Thermogravimetric Analyzer under $N_2$, respectively. Flexural testing and tensile testing were accomplished with an Instron 4505 Mechanical Tester. Impact property was determined by a Impact Elasticity Tester.

## RESULTS AND DISCUSSION

**Effect of CTBN on the curing behavior of the matrix** Figure 1 shows the DSC curve of the matrix made of BMDPM, DABPA, active diluent and epoxy, and Figure 2 show that of the matrix with addition of CTBN. Without CTBN, the onset temperature for curing reaction is 171℃, and the exothermal peak temperature is 194.85℃.With introduction of CTBN to the matrix, the onset temperature and the exothermal peak temperature are 175℃ and 200℃, respectively. By comparison, it is obvious that CTBN has little effect on the curing behavior of the matrix. Table 1 show the effect of CTBN composition on the gelation time of the modified resin. It can be concluded that the gelation time is shortened with the increase of acrylonitrile content.

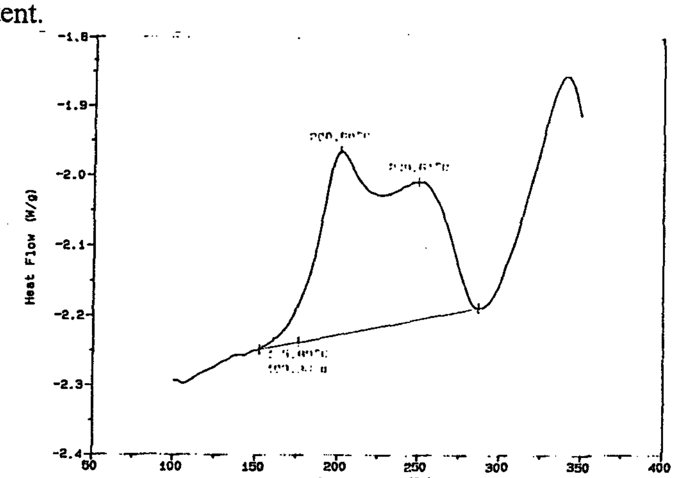


**Fig. 1 DSC curve for BMDPM/DABPA/active diluent/epoxy system**

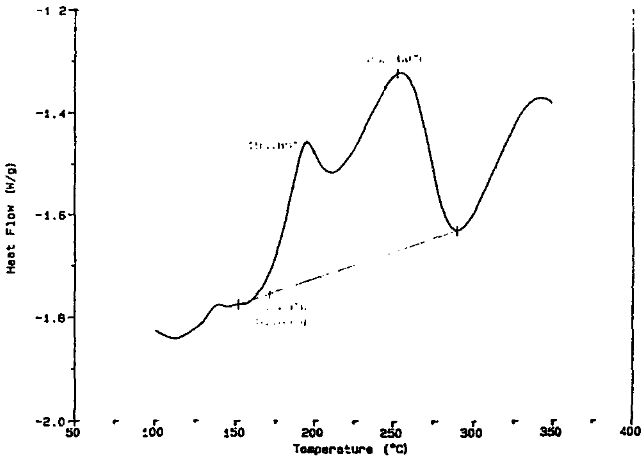


**Fig. 2 DSC curve for BMDPM/DABPA/active diluent/epoxy/CTBN system**

**Table 1 Effect of the composition of CTBN on gelation time**

| Composition, % | | 8.25 | 18.2 | 25.68 | 27.4 |
|---|---|---|---|---|---|
| Gelation time, min | 150℃ | 42.25 | 44.51 | 48.17 | 49.41 |
| | 195 ℃ | 3.6 | 3.73 | 3.9 | 3.93 |

**Effect of The Composition of CTBN on Mechanical Properties of The Modified Resin**

From table 2 we can conclude that the impact strength, tensile strength and tensile elongation have maximums during the change of acrylonitrile content from 8.25% to 27.4%, and that the flexural strength has a little loss with the increase of acrylonitrile content.

**Table 2 Effect of the composition of CTBN on mechanical properties**

| Composition, % | 8.25 | 18.2 | 25.68 | 27.4 |
|---|---|---|---|---|
| Impact strength, $KJ/m^2$ | 5.816 | 8.192 | 10.63 | 10.454 |
| Flexural strength, MPa | 108.02 | 96.11 | 95.00 | 93.85 |
| Tensile strength, MPa | 47.77 | 49.21 | 52.9 | 46.54 |
| Tensile elongation, % | 1.353 | 2.052 | 2.14 | 1.902 |

**Effect of The Composition of CTBN on Heat Tolerance of The Modified Resin** Table 3 show that the glass transition temperatures(Tg) of the modified resin are lowered from 265℃ to 250℃ and the onset decomposition temperatures are hardly lowered when the CTBN composition changes from 8.25% to 27.4%.

**Table 3 Effect of the composition of CTBN on heat tolerance**

| Composition, % | 8.25 | 18.2 | 25.68 | 27.4 |
|---|---|---|---|---|
| Tg (℃) | 265 | 254 | 252 | 250 |
| Onset decomp. temp., ℃ | 309 | 310 | 308 | 310 |

According to the above discussed, CTBN with 25.68% acrylonitrile was chosen to investigate the effect of the concentration on the properties of the modified resin.

**Effect of The Concentration of CTBN on Gelation Time of The Modified Resin** Table 4 shows the effect of CTBN concentration on the gelation time of the modified resin. With the increase of the CTBN concentration, the gelation time is shortened.

**Table 4 Effect of CTBN concentration on gelation time**

| CTBN/BMDPM, Wt% | | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|---|
| Gelation time, min | 150℃ | 67.15 | 52.85 | 48.39 | 47.93 | 46.73 | 45.33 |
| | 195℃ | 5.17 | 4.20 | 4.05 | 4.03 | 3.97 | 3.90 |

**Effect of CTBN Concentration on Mechanical Properties of The Modified Resin** We can see from Table 5 that when the weight used in the matrix increases, the flexural strength and the tensile strength decrease, and the impact strength has a maximum, while the tensile elongation increases. But the modified resin with about 5% CTBN has a good comprehensive mechanical properties.

**Table 5 Effect of CTBN concentration on mechanical properties**

| CTBN/BMDPM, Wt% | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| Flexural strength, MPa | 118.83 | 116.05 | 114.39 | 107.29 | 93.65 | 87.42 |
| Tensile strength, MPa | 62.9 | 59.99 | 59.17 | 52.19 | 45.65 | 44.3 |
| Tensile elongation, % | 1.72 | 1.92 | 2.10 | 2.43 | 2.51 | 2.76 |
| Impact strength, $KJ/m^2$ | 7.36 | 8.90 | 10.26 | 11.07 | 10.66 | 8.86 |

**Effect of CTBN Concentration on Heat Tolerance of The Modified Resin** From Table 6, it can be concluded that the CTBN concentration from 2% to 10% has not significant effect on the heat resistant property of the matrix.

**Table 6 Effect of CTBN concentration on heat tolerance**

| CTBN/BMDPM, Wt% | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| Tg (℃) | 242 | 238 | 247 | 245 | 241 | 240 |
| Onset decomp. temp., ℃ | 312 | 306 | 309 | 309 | 308 | 306 |

**Properties of The modified Resin with 5%(wt) CTBN Containing 25.68% Acrylonitrile** Table 7 show the resin properties, and Table 8 show the properties of resin laminate reinforced by T-300 carbon cloth. It is obvious that the optimized resin has good comprehensive property.

**Table 7 Properties of the optimized resin**

| Item | Temperature | Testing value |
|---|---|---|
| Gelation time | 195℃ | 4′ 14″ |
| Density, g/cm$^3$ | 25℃ | 1.27 |
| Tg, ℃ | | 247 |
| Onset decomp. temp., ℃ | | 309 |
| Flexural strength, MPa | 25℃ | 113 |
| Tensile strength, MPa | 25℃ | 59 |
| Tensile elongation, % | 25℃ | 2.4 |

**Table 8 Properties of resin laminate reinforced by T-300 carbon cloth**

| Item | Temperature | Testing value |
|---|---|---|
| Resin content, %(wt) | 25℃ | 27 |
| Density, kg/cm$^3$ | 25℃ | 1.62 |
| Flexural strength, MPa | 25℃ | 849 |
| | 130℃ | 559 |
| | 150℃ | 408 |
| Flexural modulus, GPa | 25℃ | 62 |
| | 130℃ | 55 |
| | 150℃ | 53 |
| Tensile strength, MPa | 25℃ | 700 |
| | 130℃ | 600 |
| | 150℃ | 551 |
| Tensile modulus, GPa | 25℃ | 79 |
| | 130℃ | 68 |
| | 150℃ | 70 |

## MAIN CONCLUSION

The amount of and the composition (acrylonitrile content) of the added CTBN have effect on the mechanical properties and heat tolerance of BMDPM/DABPA/active diluent/epoxy matrix. The modified resin with 5%(wt) CTBN containing 25.68%(wt) acrylonitrile can be fast cured, the flexural strength, tensile strength, tensile elongation and Tg of the modified resin are 113MPa, 59MPa, 2.4% and 247℃, respectively. The flexural strength, flexural modulus, tensile strength, tensile modulus of the laminates reinforced by T-300 carbon cloth are 849MPa, 62GPa, 700MPa and 79GPa at room temperature, while at 130℃ they are 559MPa, 55GPa, 600MPa and 68GPa.

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