STUDY ON THE MODIFIED BISMALEIMIDE

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ABSTRACT

In this paper,the experiment of using modifier B to improve the dissolvability of the prepolymer of bismaleimide/diamine is reported. The results indicate the prepolymer of bismaleimide/diamine after modified by B can be dissolved in aceton easily and the solution has enough long harmonious at room temperature. It makes convenient for preparing prepreg. Meanwhile,the thermal properties of resins have been studied by analysis method.

Keyword bismaleimide,prepolymer,dissolvability,thermal stability

INTRODUCTION

Cross-linked resins of bismaleimides yield with excellent thermal stability have been used widely. Recently,the progress of studing bismaleimide is very quickly(1). However,the extremely brittle and poor dissolvability properties of the cured resin prohibit its using to a certain degree. These disadventages have been overcome by the modification of bismaleimide prepolymer with rubber(2,3) or by chain-extended methods. The chain extented products are prepared by the Michel Addition reaction of bismaleimide with reactants such as diamines(4~6),dithiols(7~8) or allyl compound(9~10). But these modifications make their technology and thermal stability properties be reduced. Such as the modification resins can only dissolve in DMF,the decomposition and glass transition temperature are decreased. The inprovment both in the dissolvability and brittle of the resin is still an important task for the researcher all over the world.

In early 1980s,researchers found that the bismaleimide reacting with diamines could be improved its toughness in some extent,but this modified material can only dissolve in N. N-dimethylformamide(DMF),so this modification method has not been interested in recent years. In this paper,the modification of mixed systems consisting of BMI,diamine and modifier B are reported. The modifier B is a cheep chemical modifier which can improve the dissolvability of the prepolymer of bismaleimide and diamine. The results show, although the bismaleimide and modifier B do not react under the prepolymeric condition, the propolymer can dissolve in aceton easily and the cross-linked resin appears good thermal stability.

EXPERIMENT

The prepolymers prepared from N. N-bismaleimide diphenylmethane(BMI, made in Hubei Fengguang Chemical Factroy), 4, 4-diaminodipheny methane (MDA) and modifier B at several weight ratios(see Table 1)

Table 1 The formula of the resins at different percentage

HF—94	01	02	03	04	05	06	07	08	09	10
BMI	100	100	100	100	100	100	100	100	100	100
MDA	32. 5	32. 5	32. 5	32. 5	32. 5	18. 4	27. 7	36. 9	42. 5	55. 3
B	12. 3	11. 4	8. 6	2. 8	0. 0	2. 8	2. 8	2. 8	2. 8	2. 8

prepolymerization: A 500ml three-necked flask with a reflax condenser charged with BMI, MDA and modifier B which had been mixed carefully. Then, the mixture heated at 180℃, using an oil bath for 20min with stirring. After that, the prepolymer cooled to ask temperature and then charged with aceton. The amount of aceton was determined to get a 50wt% prepolymer solution.

Put the prepolymer solution into frosted glass bottle and determined the time of separation phase. Infrared(IR)spectra were recorded on a Nicolet FT-IR spectropho tometer with KBr pellets at room temperature(The sample was prepared: I. the mechanical mixture of BMI and B Ⅱ. the mixture of BMI and B after 20min at 180℃)

Thermogravimetric analysis(TGA) was carried out on a TAS-100 TGA module (made in Japan) at a heating rate of 10℃/min in air atmosphere, which the samples were prepared by HF-9401, HF-9404, HF-9405, HF-9408 and HF-9410 after curing. The curing technology is:

$$200^\circ C/2h + 240^\circ C/1h + 260^\circ C/1h$$

Differential Scaning Calorimetry(DSC) was done using a Perkin-Elmer-4 DSC module at a heating rate of 10℃/min in a nitrogen atmosphere (flow rate: 20ml/min)

RESULTS AND DISCUSSION

In Table 2 shows the dissolvation of prepolymers in aceton

Table 2 The result of the resins dissolved in aceton

HF−94	01	02	03	04	05	06	07	08	09	10
Dissolvability	+++	+++	++	+	−	+	+	+	+	+
the time of solution homogeneity	>two month				−	>two month				

+++: dissolvation at 0~5℃

++: dissolvation at room temperature

+: dissolvation at 56℃

−: can not be dissolved at any temperature

In Table 1 and Table 2 we can see that the sample of HF-9405(have no modifier B)can not be dissolved in aceton at any temperature. Therefore, it shows the samples with modifier B(HF-9401~HF-9410 except HF-9405)have good dissolvability in aceton. The amount of modifier B affects the prepolymers dissolvability in aceton greatly. In the resins of HF-9406~HF-9410, the content of modifier B is same, but the amount of diamine is different, the resin' s dissolvability in aceton is not different. It means the content of MDA does not affect the dissolvability of the prepolymeric resins. Table 2 shows that the long enough time homogeneity of the solution makes it convenient for preparing prepreg.

In order to study the reaction mechanism of modifier B in polymeric system, Fig 1 gives the IR spectrum of the mixture of BMI and B and the mixture of BMI and B after 20min treating at 180℃.

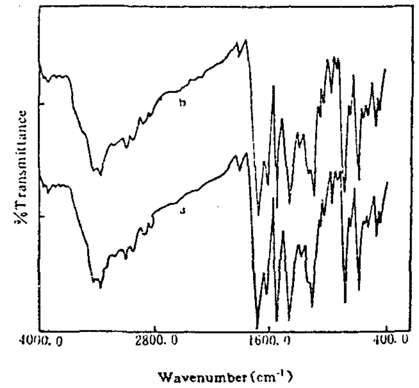
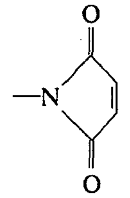
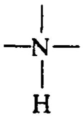


Fig. 1 The IR spectrum of the mixture BMI and B(a)and its prepolymer after 20min at 180℃(b)

Fig 1(a)and (b)shows that there is not reaction exist between BMI and modifier B under the prepolymeric condition. Therefore, we consider the mechanism of modifier B increasing dissolvability of the prepolymer is formed complex compound by the plentiful electronic material B and meleic imide group().

From Fig2 we can see, in the IR curve of HF-9404 resin there is only one feature hump at 3450cm^{-1}, it is  $-\underset{\underset{H}{|}}{\overset{|}{N}}-$ hump. The result shows the chemical reaction have been taken place betweet BMI and MDA under the prepolymeric condition.

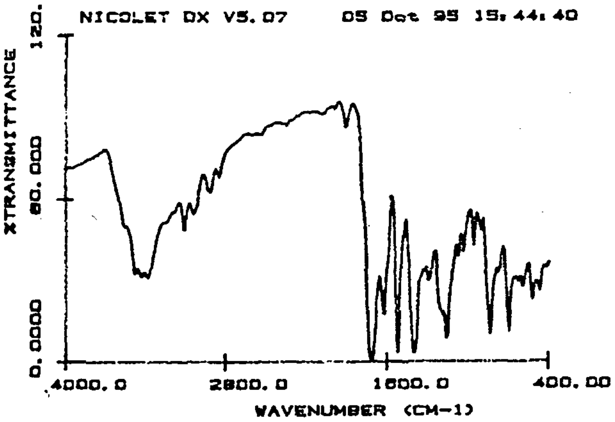


Fig. 2 The IR curve of the HF-9409 prepolymer

TGA Results

The results of thermogravimetric analysis of cured materials of HF-9401, HF-9404, HF-9405, HF-9408 and HF-9410 are showed in Fig3 and Table 3.

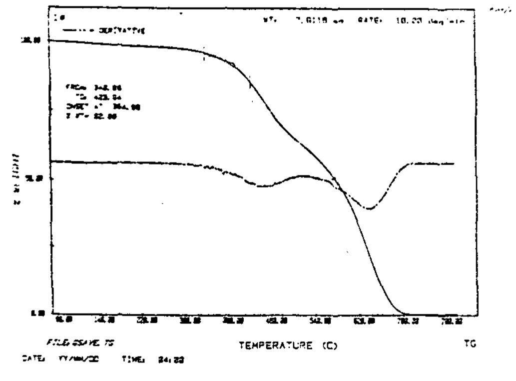


Fig 3 The TGA curve for the cured resin HF-9404

Table 3 The results of TGA for the cured resins

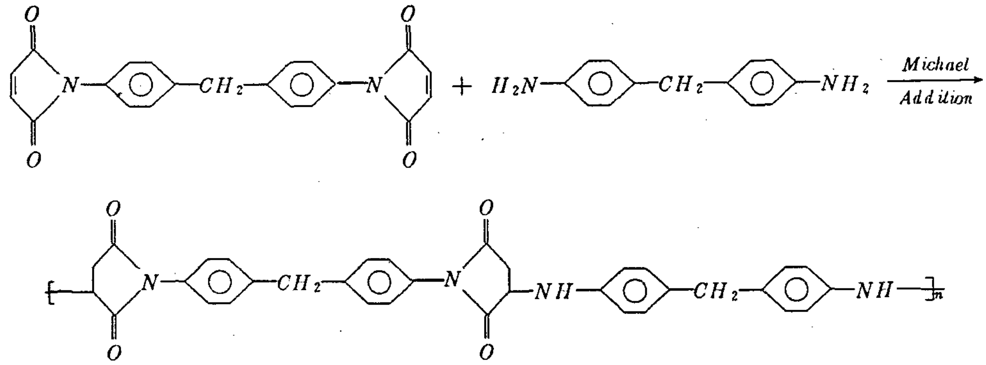
Propurties	IDT (℃)	Tmax (℃)	dα/dt (%min^{-1})	T_5	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}	T_g(℃)
HF—9401	360	476	10.2	370	382	420	460	500	580	—
HF—9404	362	478	9.7	376	390	428	466	500	582	310—323
HF—9405	364	478	9.6	378	390	427	467	501	582	—
HF—9408	355	467	10.4	362	378	4/6	451	498	578	—
HF—9410	352	458	11.3	357	370	400	439	481	573	227～244

IDT: temperature of on set weight loss
T_{max}: the fastest decomposition termperature;
dα/dt: the biggest percentage of weight loss;
T_w: the temperature of weight loss at w%;
Tg: glass transition temperature

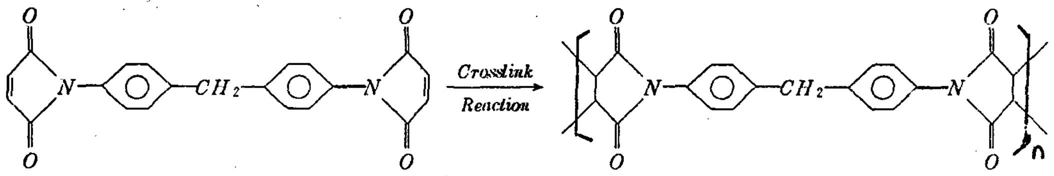
Compared TGA results and the formula of resins of HF-9401 and HF-9404 with HF-9405 show the contents of MDA is same, but the amount of modifier B is different. The contents of modifier B in HF-9401 to HF-9404 is decrease, but the T_5 of HF-9401 to HF-9405 is increase. The results indicated under the same condition of the resins have good dissolvability, the amount of modifier B must be kept at the lowest value to ensure the resin appears good dissolvability and better thermal stability.

In the resins of HF-9404, HF-9408 and HF-9410 formula, the contents of BMI and modifier B is some, but the amount of MDA is not, the result of TGA is very different. The reason is the percentage of crosslinking networks in the cured resins is different.

In preparation of prepolymers there is no chemical reaction take place between BMI or MDA and modifier B. Therefore, it is only the reaction of MDA and BMI or BMI itself be happened:



Linear structure



Crosslink Structure

Although the reaction system is very complicated, as the amount of MDA increasing, the percentage of linear structure become more and more. As we all know, the theramal stability property of crosslink structure is more perfect than that of linear structure. This is the reason of the cured resin HF-9404 thermalgravity curve(see Fig 3)has two steps: one step between 362℃ to 500℃ is the linear structure thermal decoposition reaction and the other step between 500℃ to 700℃ is the thermal decomposition reaction of crosslink structure. And from the table 3 we can see, along with the content of MDA increasing, the order of the resin's thermal resistence is .

$$HF\text{-}9404 > HF\text{-}9408 > HF\text{-}9410$$

CONCLUSION

From the above discusion, it is clear that good dissolvability prepolymer have been prepared. The amount of modifier B and MDA affect the thermal stability of the prepolymer and the amount of modifier B affect the dissolvability of the prepolymer greatly. The lower the content of modifier B and MDA in the prepolymeric system, the higher of the decomposition temperature of the cured resin.

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