P9

Study on the Curing Behavior of the Modified Bismaleimide Resin Cured at Middle Temperature

Luxia Jiang, Zhigui Xu, Yujiang Fan, Yong Lei
(Sichuan Union University, Chengdu 610065, Sichuan, PRC)

Abstract

Based on 4, 4'—bismaleimidodiphenyl methane (BMDPM), a modified bismaleimide (BMI) matrix resin, which can be cured at middle temperature (130°C) and can be dissolved in acetone, was synthesized. By means of DSC, TBA, TGA, and so on, the curing behavior and thermal stability of the matrix resin were investigated. After cured at 130°C for 4 hours and post-cured at 210°C for 2 hours, the Tg of the resin is 267.1°C, and the heat resistant temperature index is 232.3°C. So the resin can be used for aerospace tooling materials which are cured at middle temperature (130°C) and used at high temperature (180°C).

Key words: cured at middle temperature   modification
Bismaleimide resin   curing behavior

Introduction

With excellent thermal stability, good processibility and high hot-wet strength, BMI resins substitute epoxy resins step by step in aerospace and aeronautics and become candidate matrix resins for advanced composites. However, as BMI resins need high temperature (above 200°C) to cure and poor solubility (just can be dissolved in strong polar solvents with high melting point), their usage as structure composites is limited, especially as the tooling materials which need low temperature to cure and can be used at high temperature. To meet the eager demand of the tooling materials in aeronautics which are cured at middle temperature (130°C) and used at high temperature (180°C), we used aromatic diamine and multifunctional extenders to modify BMDPM. At the same time, we introduced complex additives. The synthesized resin can be dissolved in acetone, and can be used to produce tooling composite materials through autoclave at 130°C. Furthermore, the curing behavior and heat stability of the matrix resin were also studied.

Experiments

1. Materials

All the used materials are industrial products, and are used only if they are qualified.

2. Synthesis of the modified resin

According to the formulation, BMDPM and the extender were added into a reactor. After the reaction had carried out at 100~120°C for 1.5 hours, the temperature was lowered to less than 100°C, then the aromatic diamine was added. After half an hour, the temperature was lowered to below 80°C, then acetone was added slowly. The temperature was lowered to 40°C after the dissolution of one hour under reflux. Finally the additive was added, and the resin was ready for use after agitation.

3. Characterization

3.1 Preparation of samples

3.1.1 Differential Scanning Calorimetry (DSC)

The solid powder sample was obtained after drying the resin solution for 3 hours under the condition of 50°C and 700mmHg.

3.1.2 Torsional Braid Analysis (TBA)

The glass-fibre braid was treated at 400~450°C for 4~5 hours, then impregnated with resin solution (50% solid content), finally dried for 2 hours at 50°C under 700mmHg.

3.2 Test

3.2.1 Test of the solution properties of the modified resin

The test was carried out according to GB1981.

3.2.2 Test of the pre-preg flowability of the modified resin

The test was carried out according to GB5260-85.

3.2.3 Test of the degree of cure of the modified resin

The test was carried out according to GB2576-81 with the solvent N,N-dimethylformamide.

3.2.4 Differential Scanning Calorimetry (DSC)

By means of a PE DSC-7 Differential Scanning Calorimeter, the samples were heated at 10°C /min under nitrogen.

3.2.5 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) was made using a PE TGA-7 Thermal Gravimetric Analyzer. The cured sample was heated at 10°C/min under air.

3.2.6 Torsional Braid Analysis (TBA)

The test was carried out by means of GDP-2 Polymer Material Dynamical Spectrometer at 2°C/min under air.

Results and Discussion

1. Solution property of the modified resin

The solution properties of the modified BMI resin are shown in Table 1. When the solid content of the solution is about 50%, the viscosity is lower and the solution can impregnate reinforcing fibre well. The gelation time at 130°C is 240~360 seconds.

Table 1 Properties of resin solution

Property	Result
Appearance	red-brow, transparent
Viscosity (4# cup, 25 ℃), s	10~14
Solid content, %	48~52
Gelation time (little knife, 130 ℃), s	240~360

2 Effect of complex additives on the solution properties

2.1 Effect of complex additives on the viscosity of the resin solution

Fig 1 shows the relationship of the viscosity of four solutions containing different complex additives to the storage time at room temperature. It is obvious that all these four complex additives can make the resin cure at 130°C, but their activities at room temperature differ a lot from each other. The solutions containing A and B complex additives

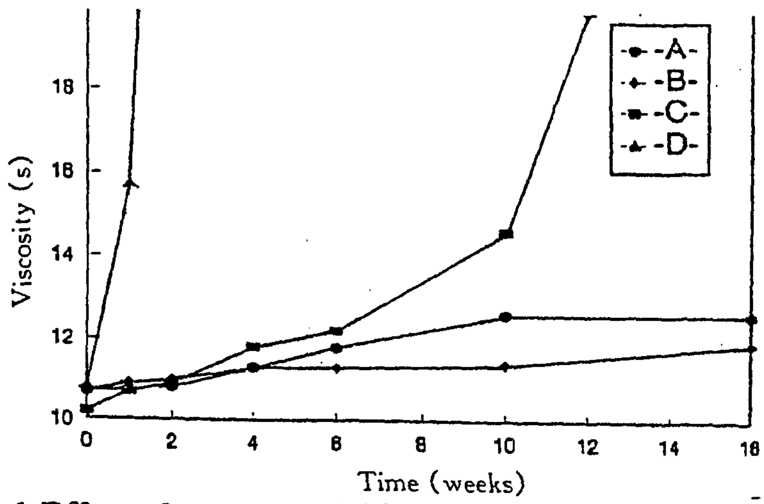

Fig 1 Effect of complex additives on the viscosity of the resin solution

respectively are stable at room temperature, and their viscosity has little change with the increase of the storage time and is still low after 4 months. But complex additive C and D have high reactivity, and viscosity of their solution rises rapidly with the storage time.

2.2 Effect of complex additives on the gelation time of the resin solution

Fig 2 shows the relationship of the gelation time of four solutions containing four different complex additives respectively to the storage time at room temperature . From the figure we can see that the initial gelation time at 130°C of these four solution differs little from each other, but with the storage time increasing , the gelation time of the solution

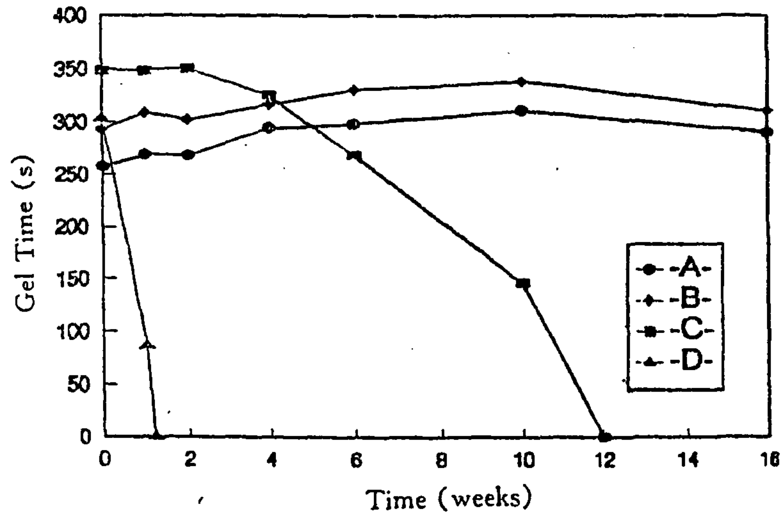

Fig 2 Effect of complex additives on gelation time of resin solutions

containing C and D additive shortens fast, especially the latter which begins to gelatinize after 10 days. However, after 4 months the gelation time of the solution containing A and B additive almost seems unchanged.

3. Curing behavior of the modified BMI resin

3.1 Analysis of the curing dynamics of the modified BMI resin

Fig 3, the TBA spectrum of the uncured resin, shows that the curing reaction comprises two phases. Between 110~160°C, the relative rigidity of the resin increases obviously with the rising of temperature;

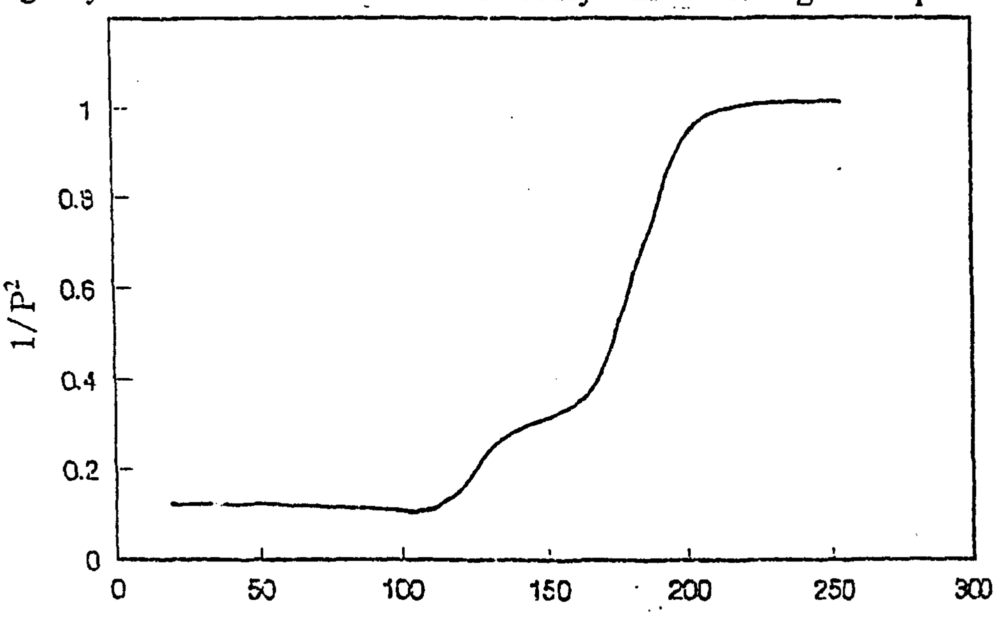

Fig 3 TBA curve of the uncured resin

between 160~200°C, the crosslinking is kept on and the relative rigidity increases very rapidly with the rising of temperature; after 200°C the curing is finished and the relative rigidity does not increase any more.

3.2 Curing technology of the modified BMI resin

Fig 4 is the curve of the change of the degree of cure of the modified resin with the increasing of curing time at 130°C. Before 3 hours the curing of the modified resin at 130°C runs very fast, but after 3 hours runs slowly. After 4 hours at 130°C, the degree of cure can be as high as 90%, and after 6 is near 92%.

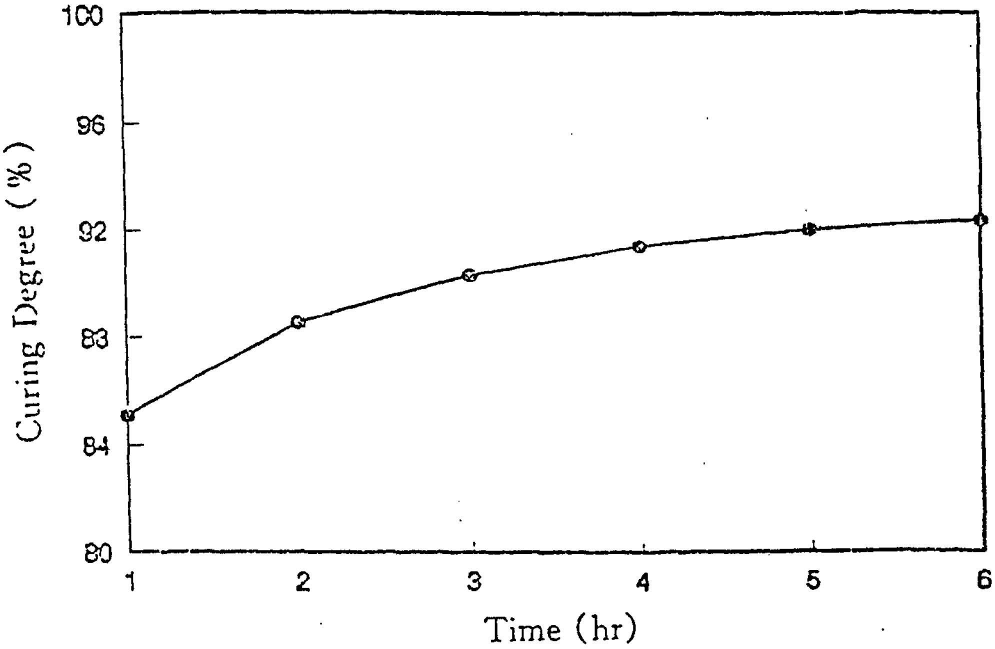

Fig 4 Relationship of degree of cure vs curing time at 130 ℃

The data about the curing under different conditions is shown in Table 2. The data shows that the curing reaction completes mainly during the first stage, and the degree of cure can be as high as 90%. In the second stage, the curing reaction is slower. The completeness of the curing reaction can be achieved by raising the curing temperature, and it comes true after 4 hours at 200°C. According to the discussed above, as well as the TBA spectrum, the curing technology, 130°C/4 hours, of the modified resin can be established, as well as the technology of post cure: 200°C/4 hours and 210°C/2 hours.

Table 2 Degree of cure at different conditions

Item	Pre-cured	Post-cured				
Temperature, ℃	130	130	160	180	200	210
Time, hour	4	2	4	6	4	2
Degree of cure,%	91.4	92.3	96.8	99.0	100.0	100.0

3.3 Study of the curing dynamic of the modified BMI resin

Fig 5 is the DSC curve of the modified resin. From the curve, the temperature range of curing is between 90.0~215.0°C, which can identified by TBA analysis . The temperature peak of curing is 155.3°C , and ∇H of the curing reaction is -295.1J/g. The curing peak is

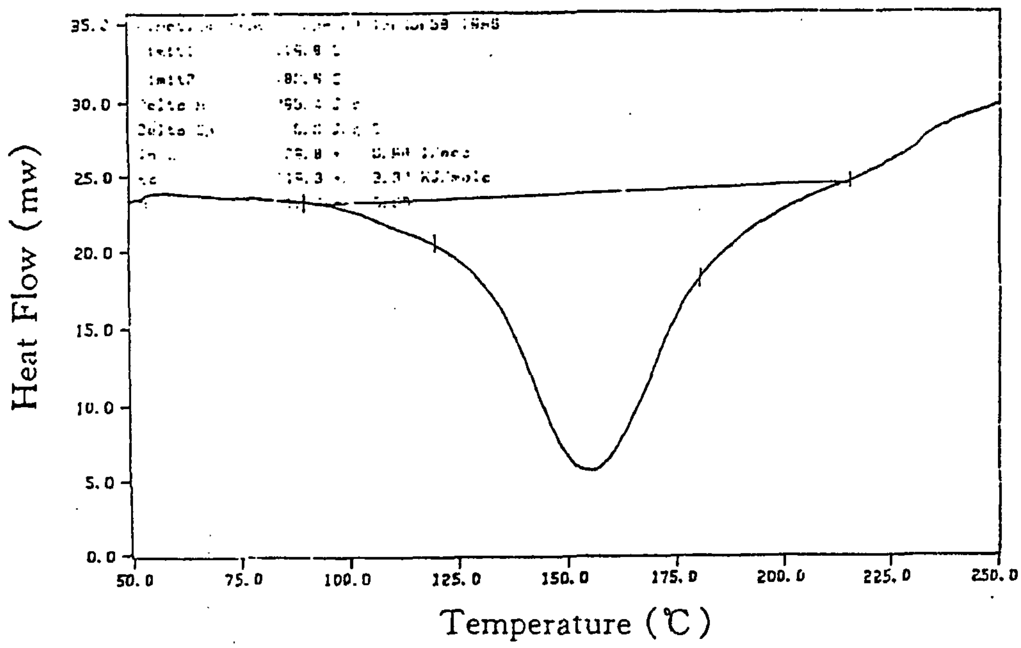

Fig 5 DSC curve of the uncured resin

wide and unsharp, which shows that the temperature range of curing of the modified resin is broad, and that the reaction is moderate, and that the processing range is also wide. According to the DSC and the corresponding formulations, we can calculate the reaction degrade and relative active energy of the modified resin, which are 1.77 and 119.3KJ/mol, respectively.

Fig 6 shows the relationship of the curing time of the modified resin to the curing temperature when the degree of cure is 50% , 60% , 70% , 80%, and 90% , respectively. It can be found that when the degree of

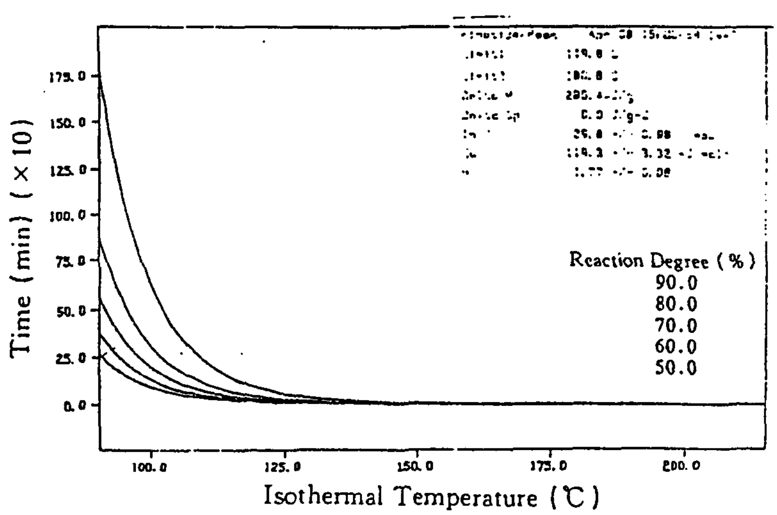

Fig 6 Relationship of curing time vs temperature

cure is certain, the curing time is shortened with the rising of the curing temperature.

Fig 7 shows the relationship of the degree of cure of the modified resin to the curing time at 100°C, 125°C, 150°C, 175°C, and 200°C, respectively. It is obvious that the degree of cure increases with the increase of the curing time at certain temperature.

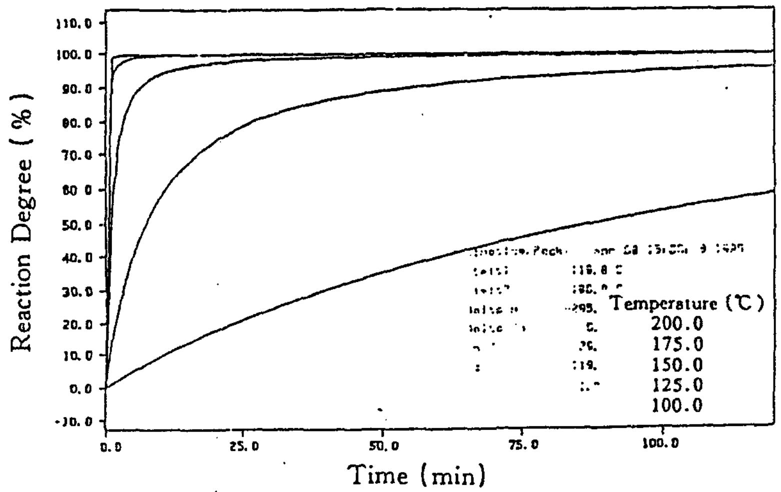

Fig 7 Retationship of degree of cure vs curing time

Fig 8 shows the relationship of the degree of cure to the curing temperature when the curing time, such as 20 minutes, 40 minutes, 60 minutes, 80 minutes, and 90 minutes, is certain. The result shows that when the curing time is certain, the degree of cure increases with the rising of the curing temperature.

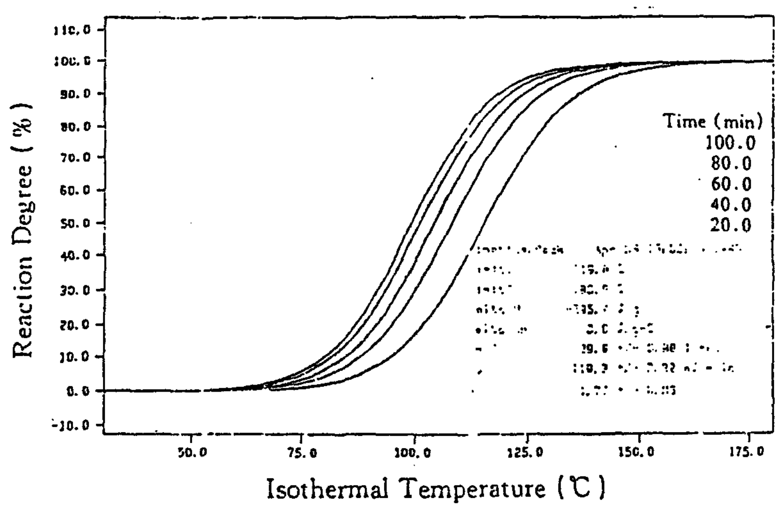

Fig 8 Relationship of degree of cure vs curing temperature

4. Thermal stability of the modified BMI resin

The value of Tg and thermal gravimetric data of the modified resin were obtained by DSC and TGA of the cured resin. Fig 9 is the TGA curve and Table 3 shows the data of TGA . According to the figure . it can be concluded that the temperature of decomposing of the resin is over 300°C, and that there exist two stages, 390~440°C and 570~770°C, during which the speed of losing weight is fast. According to the data in Table 3, the heat resistant temperature index, 232.3°C, can be figured out by statistic method.

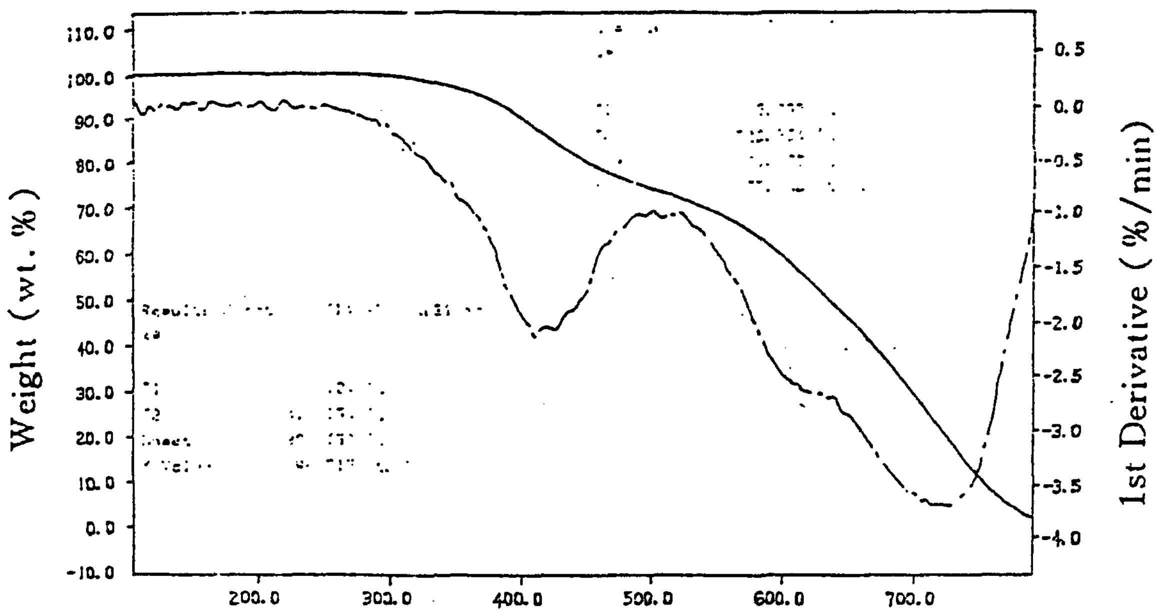

Fig 9 TGA curve of the cured resin

Table 3 TGA data

Loss weight, %	5	10	15	30	50
Temperature, ℃	370.7	403.3	427.0	543.0	634.3
Heat-resistant temperature index, ℃	232.3				

Fig 10 is the DSC curve of the cured resin. The figure shows that the Tg of the modified resin is 267.1°C.

Conclusion

By means of the technology of melting prepolymerization and solution prepolymerization of the materials of aromatic diamine and multifunctional extenders and with the introduction of complex additives, we synthesized a modified BMI resin based on 4, 4'—bismaleimidodiphenyl methane (BMDPM). After cured at 130°C for 4 hours and post-cured at 200°C for 4 hours and 210°C for 2 hours respectively, a high temperature resistant matrix resin , which can be used at 180°C

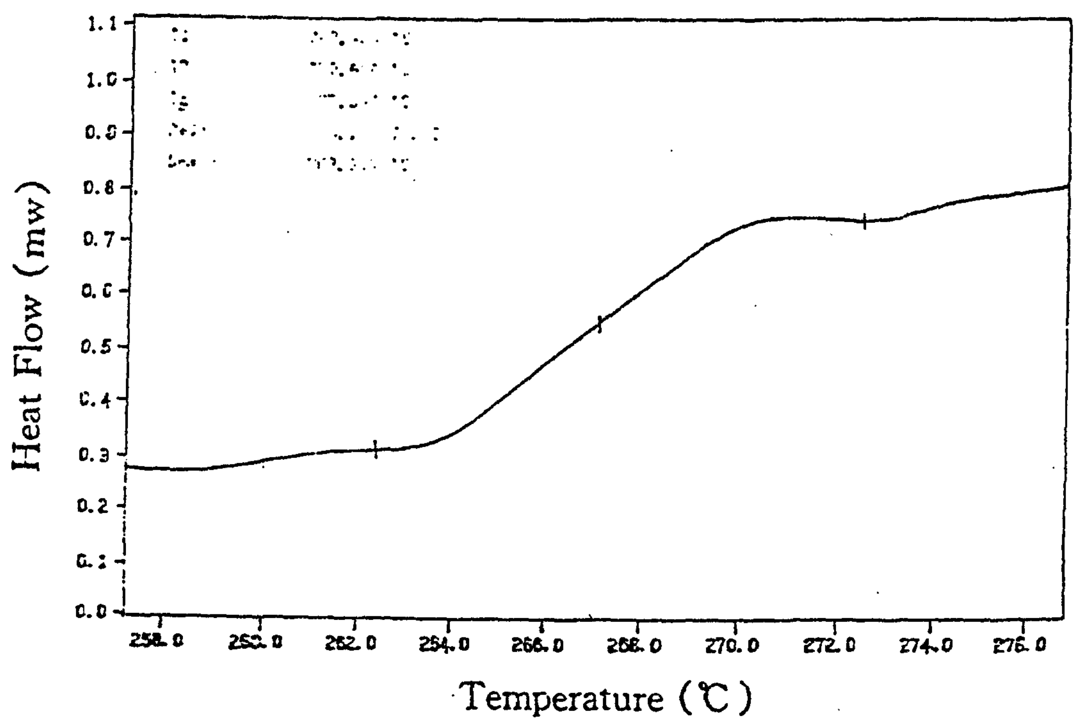

Fig 10 DSC curve of the cured resin

for long time, can be obtained. The resin is suitable to be used as advanced composites for aeronautic tooling materials which are cured at middle temperature (130°C) and can be used at high temperature (180°C).

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