Study on Synthesis and Performance of Rosin-Derived Polyamide as Epoxy Curing Agent

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Abstract— **Rosin is an abundantly available natural product. The rosin-based polyamide (RBPA) was synthesized and studied as epoxy curing agent in the paper. The performance of thecured products of epoxy resin/RBPA composites was characterized by FT-IR, TGA and tensile machine. It was found that epoxy resin/RBPA system can cured completely at mass ratio of 100:51 under the condition of room temperture for 6 h, and then 80 ℃ for 4 h, the shear strength of epoxy resin/RBPA system was 21.6 MPa, the thermal decomposition temperatures of the cured products of the cured system was 343.0 ℃, glass transition temperatures was 146.6 ℃. Rosin-based polyamide has a great potential to replace some of current petroleum-based compounds in the synthesis of epoxy curing agents.**

Index Terms— **epoxy resin; maleic anhydride; diethylenetriamine; heat-resistance; differential scanning calorimetry**

I. INTRODUCTION

Epoxy resin, as a typical representative of the thermosetting resin, has been widely used because of its excellent properties such as unique combination of property, chemical stability, electric insulation performance and workability[1]. This makes it a viable products for various industrial applications such as coatings, casting materials, fiber reinforced composites, adhesive, molding compound.

Rosin is an abundantly available natural product from the exudation of pines and conifers. Rosin acids are similar to many aromatic compounds in molecular rigidity because of the large hydrogenated phenanthrene ring structure[2-5]. The carboxy group and conjugated double bond in rosin molecular with high activity sin can be easy to isomerization[6-9], such as addition, disproportionation, hydrogenation,

polymerization, aminolysis, esterification, salt formation, decarboxylation reaction[10-13]. Therefore, rosin and its derivatives can be modified to prepare a series of polymer materials and additives. Maleopimaric acid anhydride, a semisynthetic-organic monomer, is prepared with levopimaric acid from rosin by Diels-Alder reaction with maleic anhydride. As a derivative of rosin, maleopimaric acid anhydride not only possesses favorable biodegradability and biocompatibility, which has been widely used in medicine, nonpoisonous coating of environmental protection[14-15], but also has ability to synthesize good thermal endurance products for the phenanthrene structure.

In this manuscript, the synthesis and properties of a new kind of rosin-based curing agent with good heat-resistant were reported, the curing kinetic behavior of epoxy resin/rosin-derived polyamide, and mechanical properties of the cured product were also investigated. The result shows that the curing agent rosin-derived polyamide possesses excellent properties of heat-resistance and mechanical performance. Moreover, as a curing agent with good heat-resistant, the rosin-based polyamide which was synthesized in the paper can be cured with epoxy resin under a gentle condition, it will be found wide application in micro-electronics[16], electronic packaging fields.

II. MATERIALS AND METHODS

Materials
Epoxy resin (E-51), with an epoxy value of 0.51 mol/100 g, was obtained from Wuxi Resin Factory; abietic acid (75 %), maleic anhydride (powder, 95%), p-toluene sulfonic acid, were obtained from Aldrich; ethanol(AR), used as solvent, was supplied by Sinopharm Chemical Reagent Co., Ltd. Diethylenetriamine(99.9 %), was obtained from HUNTSMAN company of America.

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Characterization

^{1}H-NMR spectrum was recorded using a Bruker 300 MHz spectrometer at room temperature with DMSO as solvent. Fourier transform infrared spectra were recorded with Nicolet NEXUS 670 FT-IR spectrometer. The cured product was scanned from 4000 to 680 cm^{-1}.

Thermal stability was analysed by non-isothermal differential scanning calorimetry (DSC) on Diamond DSC Analyzer with the scanning range from 25 ℃ to 700 ℃ at a heating rate of 10 ℃/min, and glass transition temperature of the cured product was estimated with the scanning range from 25 ℃ to 300 ℃ at the heating rate of 10 ℃/min,

Non-isothermal DSC curves for curing kinetic behavior were obtained at heating rate 5, 10, 20, 40 ℃/min respectively.

Shear strength test was performed on a electronic universal testing machine equipped with a 3 kN electronic load. The test was conducted at a crosshead speed of 1 mm/min, five replicates were tested for cured system to obtain average values of the properties.

Synthesis of Maleopimaric acid anhydride

To a 250 ml four-necked round flask equipped with a polyfluortetraethylene stirrer, water separator, thermometer and N_2 conduit, was charged 50 g of abietic acid, 9.8 g of maleic anhydride, 1.92 g of p-toluene sulfonic acid and 30 g of glacial acetic acid. After feeding N_2 for 15 min, heated till the materials melted down essentially, started to stir and heated up continued to 180 ℃, temperature controlled by the amount of glacial acetic acid in the system, kept 180 ℃ for 4 h to complete the isomerization from the abietic structure to the pimaric structure under the protection of N_2, then dropped to 110 ℃ and 100 ml glacial acetic acid was added, stirred for cooling down till to the room temperature. Collect white crystalline of raw maleopimaric acid anhydride product by suction filtration. After recrystallization of the raw product by acetic acid, white acicular crystal of maleopimaric acid anhydride was gained by vacuum desiccation operation.

Synthesis of Rosin-derived polyamide (RBPA)

To a 250 ml three-neck flask equipped with a polyfluortetraethylene stirrer, reflux condenser and thermometer, was charged 100 g of maleopimaric acid anhydride and 100 g of ethanol, heated to boiling state till maleopimaric acid anhydride was dissolved thoroughly in ethanol. In a 250 ml four-necked round flask equipped with a polyfluortetraethylene stirrer, reflux condenser, thermometer and constant pressure drop funnel, 103.2 g of diethylenetriamine was heated to 140 ℃, maintained at this temperature, spotted the above-prepared maleopimaric acid anhydride-ethanol solution drop by drop in 0.5 h while distillation operation was going on, after the end of drop wise process, turned the distillation unit to backflow setting and maintained for 2 h, then the system was heated to 210 ℃ gradually and continued at this temperature for another 3 h. In the end, pumped air into vacuum by water circulating pump for 0.5 h, the brown semisolid product obtained was RBPA.
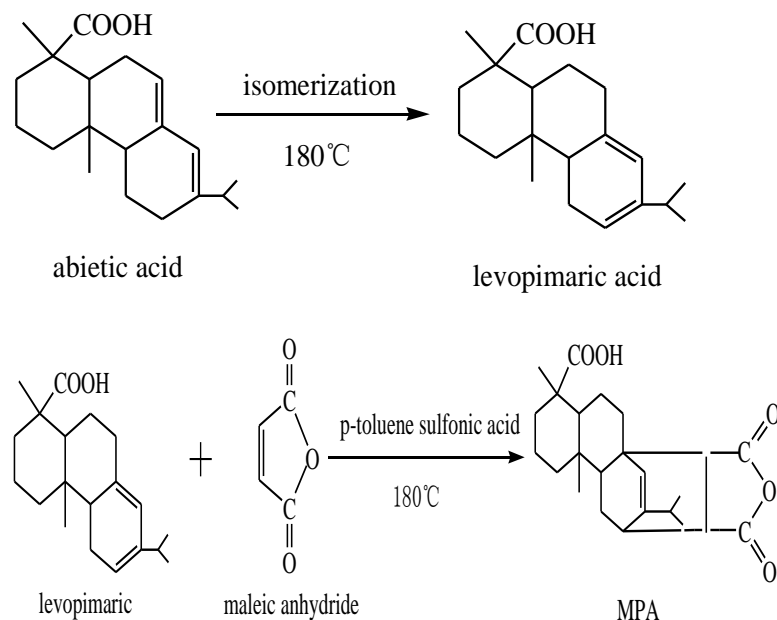
Curing procedure

Epoxy resin and RBPA were mixed thoroughly on the following mass ratio: epoxy resin: RBPA=100:51, then did curing kinetic analysis and curing experiment.

III. RESULTS AND DISCUSSION

Synthesis and characterization of maleopimaric acid anhydride

The synthesis route and chemical structures of maleopimaric acid anhydride were outlined in Scheme 1. The synthesis of maleopimaric acid anhydride involved two steps: isomerization reaction and Diels-Alder reaction. Because only levopimaric acid can take the Diels-Alder reaction, other isomeric rosin acids can be converted to levopimaric acid through isomerization under elevated temperatures[7], raw abietic acid was first heated at 180 ℃ for 4 h to complete the isomerization from abietic structure to pimaric structure in the synthesis of maleopimaric acid anhydride. Maleopimaric acid anhydride was prepared by reacting levopimaric acid with maleic anhydride under p-toluene sulfonic acid. The formation of maleopimaric acid anhydride was verified by FT-IR (**Fig. 1**). The appearance of characteristic peak at 1842.03 cm^{-1} was the stretching vibration absorption peak for carbonyl group of acid anhydride, and 1080.59 cm^{-1} for C–O–C stretching vibration absorption peak.

Scheme 1. Synthesis route of maleopimaric acid anhydride

The chemical structure of maleopimaric acid anhydride was confirmed ^{1}H-NMR (**Fig. 2**). In the Fig 2, $\delta 12.2$ was the H of —COOH, $\delta 5.5$ was the unsaturated H of C=CH that produced by Diels-Alder reaction, $\delta 3.3$-0.9 were the H of aliphatic hydrocarbon and alicyclic hydrocarbon. It was in complete agreement with reference [17].
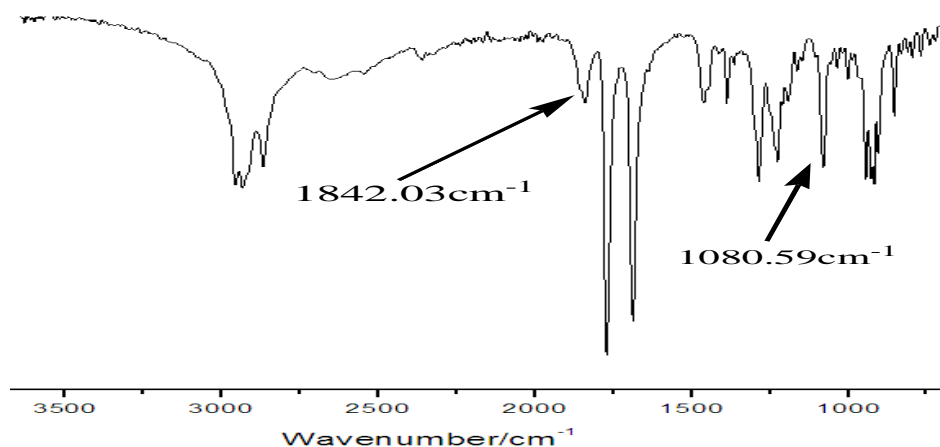
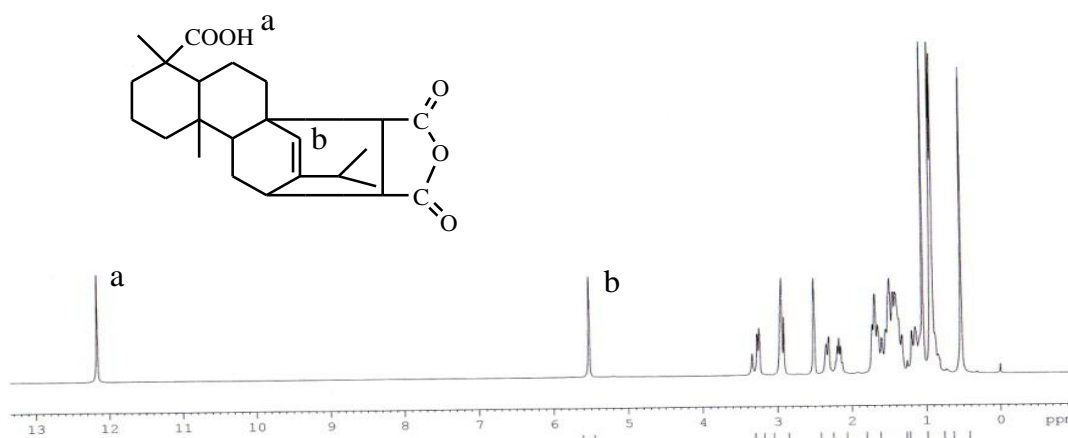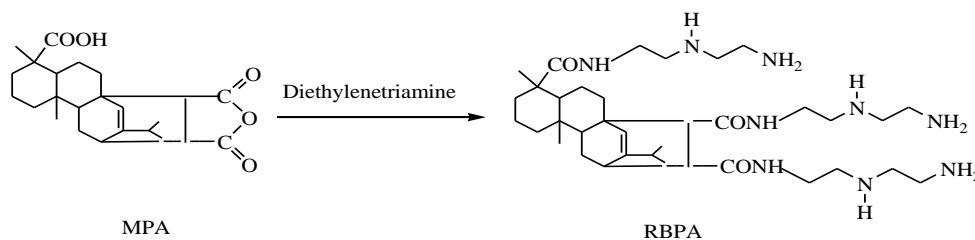**Fig. 1.** FT-IR spectrum of maleopimaric acid anhydride

Fig. 2. ^{1}H-NMR spectrum of maleopimaric acid anhydride

Synthesis and characterization of rosin-derived polyamide
The synthesis route and chemical structures of rosin-derived polyamide was outlined in Scheme 2. Diethylenetriamine reacted with maleopimaric acid anhydride by salt-forming reaction for 2 h at 140 ℃. Then the system was heated up to 210 ℃ gradually and continued at this temperature for another 3 h for dehydration reaction, vacuumization operation for 0.5 h, we got rosin-derived polyamide, the amine value of product was 371.8 mg/g. **Fig. 3** gave the IR spectrum of RBPA that prepared by maleopimaric acid anhydride with diethylenetriamine. Curve A was the spectrum of maleopimaric acid anhydride, curve B was diethylenetriamine and curve C was rosin-derived

polyamide. In the curve A, 1842.03 cm^{-1} was the extension vibration absorption peak of carbonyl group of anhydride, 1080.59 cm^{-1} was the extension vibration absorption peak of C–O–C of anhydride; In the curve B, 3295 cm^{-1}was the absorption peak of primary amine, after the amidation reaction, the absorption peak at 1842.03 cm^{-1} and 1080.59 cm^{-1} were disappeared basically, the absorption peak of carbonyl group of amide was turned out at 1690 cm^{-1}, as curve C indicated. From Fig. 3, we can know that, amidation of maleopimaric acid anhydride and diethylenetriamine was completed, the rosin-derived polyamide was gained.

MPA   RBPA

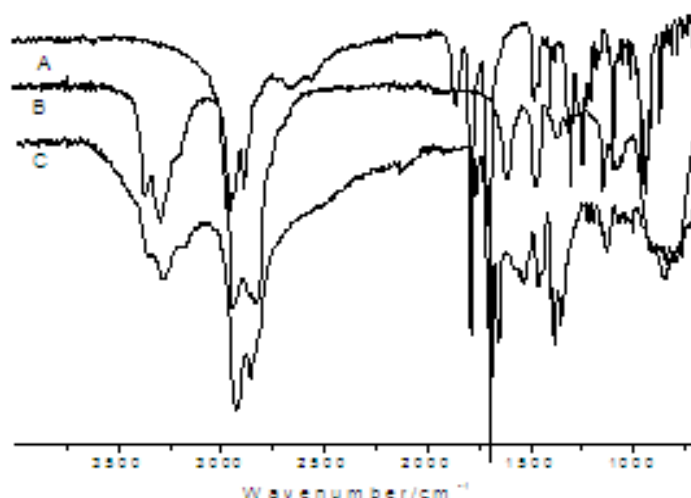**Scheme 2**. Synthesis route of rosin-derived polyamide

Fig. 3 FT-IR spectrum for synthesis of rosin-derived polyamide
A: maleopimaric acid anhydride B: diethylenetriamine C: rosin-derived polyamide

The mass ratio and curing time of epoxy resin/ RBPA system
Epoxy resin and RBPA were mixed thoroughly on the following mass ratio: epoxy resin: RBPA=100:40, 100:51, 100:60 respectively, cured at room temperature for 6 h, and then at 80 ℃ for 4 h. **Fig.4** showed the TG and IR curve of

the cured products at different mass ratio. As Fig. 4 shown,

we can conclude that the cured product (epoxy resin: RBPA=100:51) has the best heat resistance, the absorption peak at 3295 cm^{-1} and 915 cm^{-1} were disappeared basically in IR spectra. So the mass ratio of epoxy resin and RBPA was 100:51.
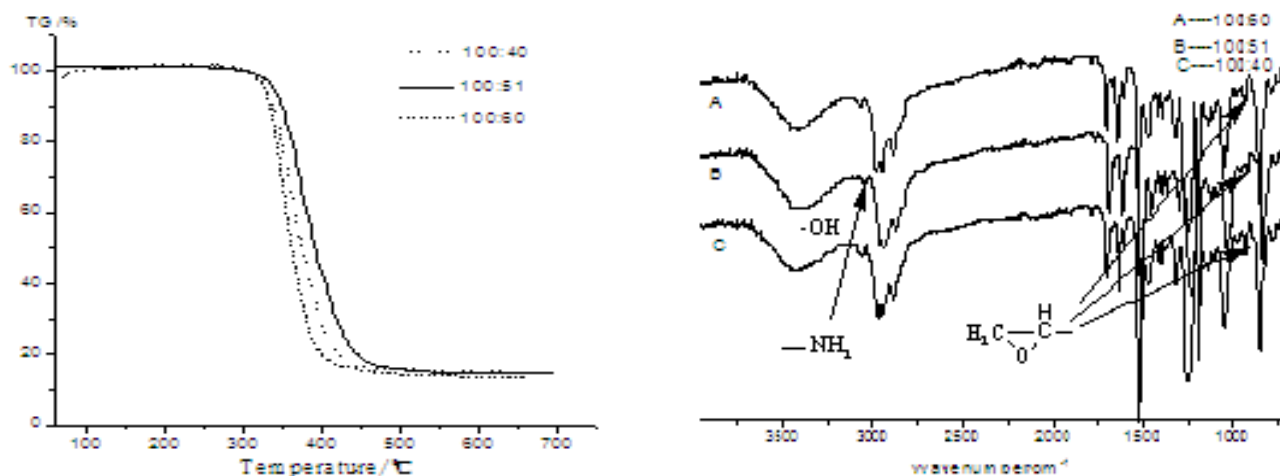

Fig. 4 TG and IR analysis of cured product of epoxy resin/rosin-derived polyamide
at different mass ratio

When the epoxy resin and RBPA were mixed thoroughly on the following mass ratio: epoxy resin: RBPA=100:51, FT-IR spectra of epoxy resin/RBPA at different curing time was shown in **Fig.5**. In the curve a, 3295 cm^{-1}was the stretching vibrational absorption peak of primary amine, 915 cm^{-1} was the characteristic absorption peak of epoxy group of epoxy resin. After curing for 6 h at room temperature, the two absorption

peaks above were weaken, the absorption peak of −OH at 3453 cm^{-1} appeared weakly, as shown in the curve b. With the increase of curing time, the peak at 3295 cm^{-1} and 915 cm^{-1} wore off, the absorption peak at 1842 cm^{-1} and 1081 cm^{-1} were disappeared basically for 4 h at 80 ℃, as shown in the curve d. The result indicated that the epoxy resin/RBPA system can fully cure at room temperature for 6 h, and then at 80 ℃ for 4 h.
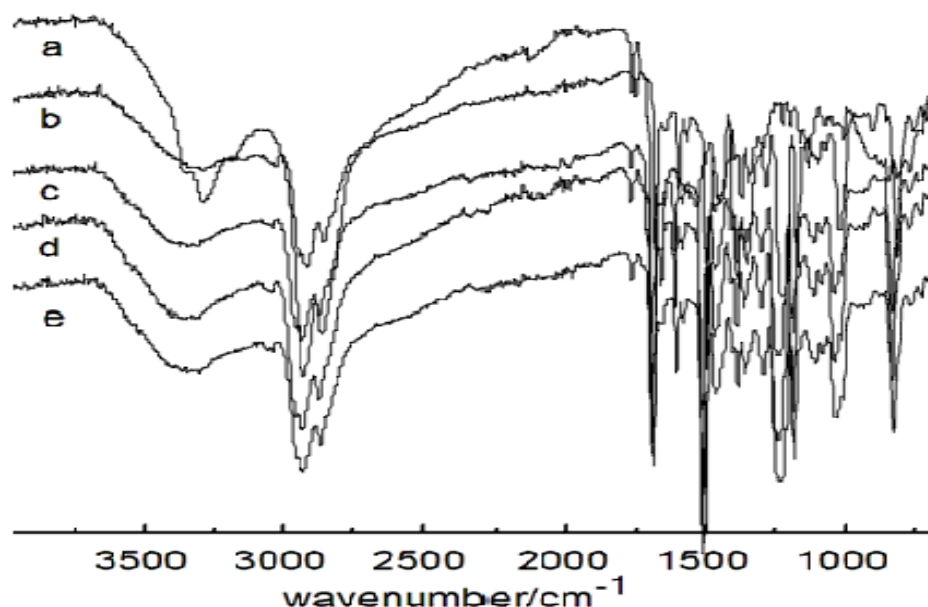
Fig.5 FT-IR spectra of epoxy resin/RBPA at different curing time

Heat-resistance analysis
Thermal stability

Fig.6 showed that the TG curve of the thermal stability of epoxy resin cured with rosin-derived polyamide, the scan rang covered 25~700 ℃. It was clear from Fig. 6 that the weight loss interval was in 343~410.2 ℃, and in this section, the loss percent of weight was 82.99 %; the decomposition rate of system increased gradually in 343~371.3 °C, when the fundamental chain started to break down, the rate was to be the maximum at 371.3 ℃. After that, the rate reduced and halted at 410.2 ℃, the mass of the system did not change significantly.
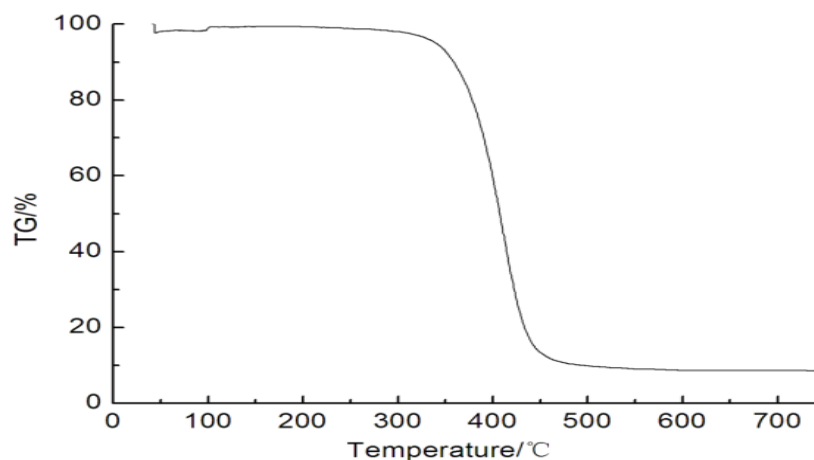

Fig.6 TG analysis of cured product of epoxy resin/ RBPA

Glass transition temperature

Glass transition temperature (T_g) of epoxy resin/RBPA was obtained from the inflection of the DSC curve. The DSC curve(**Fig.7**) showed the T_g for epoxy resin/RBPA was 146.6 °C. T_g for the epoxy cured with aliphatic amine curing agent was only 114.4 °C as shown in Fig.8. This result indicates that the introduction of the large-scale phenanthrene ring into the curing agents improves markedly the thermal stability of the cured system. This result indicates that epoxy resin /RBPA system has higher glass transition temperature, mainly due to containing more rigid structure.
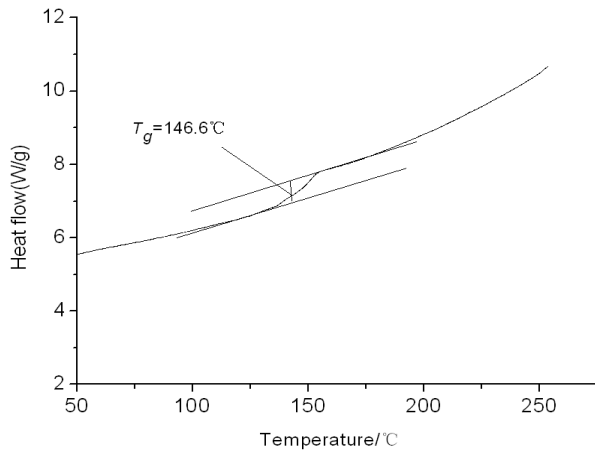
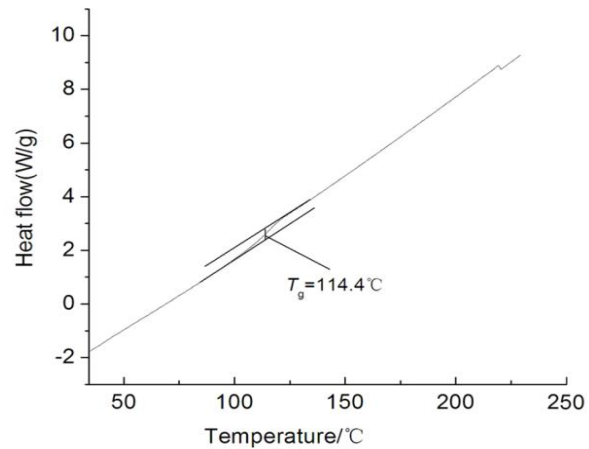**Fig. 7** Glass transition temperature(T_g) of epoxy resin/ RBPA System

Fig. 8 Glass transition temperature(T_g) of epoxy resin/ MeTHPA system

Shear strength test

The chemical structure of the curing agent depends significant on the morphology and crosslink density of its network, affecting its mechanical properties. Five replicates were tested for the cured system of epoxy resin/rosin-derived polyamide to obtain average values of shear strength, as was summarized in **Table 1**, epoxy resin/ C_{21} diacid polyamideas in **Table 2**.

Table 1
Shear strength of the cured system of epoxy/ RBPA

resin/ RBPA	shear strength/ MPa	average shear strength/ MPa
1[#]	21.16	
2[#]	20.85	
3[#]	22.85	21.6
4[#]	22.0	
5[#]	21.23	

Table 2
Shear strength of the cured system of epoxy/ C21 diacid polyamideas

resin/ C21 diacid polyamideas	shear strength/ MPa	average shear strength/ MPa
1[#]	9.85	
2[#]	10.36	
3[#]	11.28	10.6
4[#]	10.54	
5[#]	10.97	

The results shows that the average shear strength for the epoxy resin/RBPA was 21.6 MPa, for the epoxy resin/aliphatic amine system was 10.6 MPa. It was likely that maleopimaric acid anhydride was a three degrees of functionality, the number of the reactive hydrogen which introduced into the rosin-derived polyamide by amidation were more than the single aliphatic amine, so generated more polar groups after the curing reaction to improve the shear strength with Fe plate, and at the same time, the introduction of diethylenetriamine which played the role of soft segment can cause segment motion of the material under load of certain degree, both the two factors resulted in the good shear strength of the system of resin/RBPA.

IV. CONCLUSIONS

Rosin-derived polyamide was synthesized and studied for epoxy curing. The epoxy cured with rosin-based curing agent displayed high shear strength, modulus. The hydrogenated phenanthrene ring structure of rosin and its derivatives is a rigid entity.

Therefore, the thermal stability of the cured epoxy has remarkably improved compared with traditional curing agents. These results indicated that the rosin-derived polyamide could be used as an important alternative feedstock to petroleum-based analogs for the synthesis of epoxy with higher thermal stability. The rosin-derived polyamide prepared in this paper expands the curing agent product offerings and alleviates the oil crisis to some extent. In additon, it provides theoretical references for deep-processed of rosin in the future.

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