ANALYSIS OF THE ENDOTHERMIC BEHAVIOR IN THE CURING PROCESS OF RESOLE

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SUMMARY: This paper analyzes the behavior of resole by DTA and TG, especially the endothermic behavior in the curing process. Between 130 and 160 , there are one or several endothermic peaks when resole is curing. They are the characteristic peaks of curing behavior, which can be used to identify the curing reaction and describe the flowing feature of resole. In this temperature range, the weight loss of the resole sample is high. Oxides or hydroxides of Ca and Mg can accelerate the curing process and decrease the temperature of exothermic and endothermic peaks in the curing process of resole. The amount is 10% to 15%. The endothermic peaks can be used to determine the process parameters of phenolic resole composites. In the process of phenolic SMC (P-SMC), the molding temperature shall be 20~30 above the endothermic peak's temperature of resole on the DTA and TG thermographs.

KEYWORDS: resole, curing endothermic peak, differential thermal analysis (DTA), thermalgravimetric analysis (TG)

INTRODUCTION

Resole could be used to manufacture the phenolic composite by winding, SMC, pultrusion and RTM, etc. The products have excellent properties, for instance, flame resistance, low smoke and toxicity when burning, as well as high strength retention under high temperature so that they have been widely used in many fields such as transportation, construction and so on.

The thickening and curing behavior of resole have been reported extensively in the literatures in recent years [1~4]. Phenolic sheet molding compounds (P-SMC) have gradually become important and used to industrial products. But, it is very necessary to study curing behaviors of resole under high temperature in order to suit various processes and obtain products of good properties. The previous papers on this subject were almost emphasized on exothermic curing behavior and change of structure, few on curing endothermic behaviors in the curing process. However, the curing endothermic behavior was related to the quality of products made of resole, and also important for process of resole in high temperature as the curing exothermic behaviors.

The object of this paper was to study the curing behaviors of resole with DTA and TG, focusing on the importance of the endothermic curing process analysis, and applying in determining the process parameters in molding of phenolic SMC.

EXPERIMENT

Preparation of Resole

Formaldehyde-Phenol (F/P) mole ratio was 1.2~2.0, using $Ba(OH)_2$ as catalyst with mole ratio to phenol 0.05. The mixture was charged in a 3-L three-necked flask fitted with stirrer, thermometer and refluk condenser, reacted at 60~80 for 1.5~3h in a water bath. Resole was obtained after the condensation reaction, neutralized with hydrochloric acid, and dehydrated under vacuum. Its pH value was 7.0±0.5, viscosity about 1000cps(25) and gel time 140~180s/150 .

Basic Curing Catalyst

Basic curing catalysts used were $Ca(OH)_2$ and MgO (A.P.). The amounts of catalysts added were from 5% to 15%(wt) by resin content.

Thermal Analysis of Curing Behavior

Differential thermal analysis (DTA) were performed with L_{CT}-1 DTA instrument made by Beijing Optical Equipment Plant. A sample of 15~20mg was placed on a platinum sample pan. Aluminum sample pans were not used to avoid the interaction with basic curing catalyst in resin. Then samples were heated at the rate of 5 /min. The reference sample was Al_2O_3.

RESULTS AND DISCUSSIONS

Curing Behavior of Resole

As known to all, resole could be cured by means of heating. When the resin was curing, heat was emitted and condensed water was released. These caused several endothermic and exothermic peaks appearing on the DTA thermograms, and a weight loss was also observed on TG curves. A typical thermogram of resole was shown in figure 1. From the figure 1, it could be found that the curing temperature was about 100 to 190 . In this temperature range, the curing heat was emitted and condensed water was released so that one or several endothermic peaks appeared in the process.

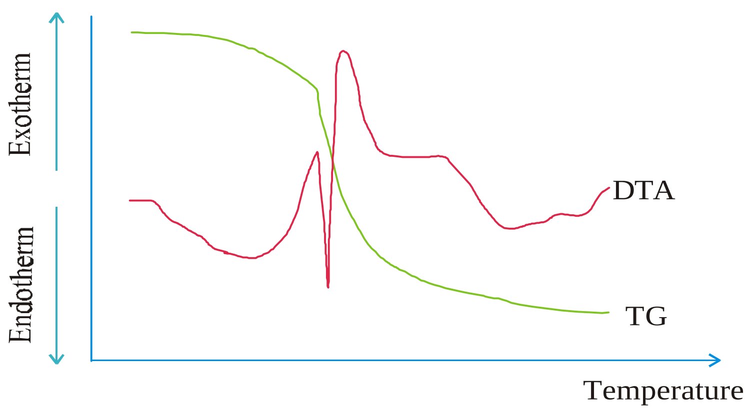


Fig.1: DTA and TG thermograms of resole

As shown in figure 1, the curing behavior of resole could be divided into three stages:

1. When the curing temperature was below about 100 , there was only one volatile endothermic peak in DTA curve and a small weight loss according to TG curve. The resole almost didn't begin reaction.

2. When temperature was raised to between about 100 and 190 , the weight loss was obvious and curing reaction almost completed in this temperature range. There were two exothermic peaks observed, one was in about 100 to 135 , the other about 155 to 190 . Between 135 and 155 , there were one or several sharp endothermic peaks, and the weight loss rate rose abruptly just in the temperature range, due to the loss of condensation water.

3. Exothermic peaks appearing above 190 were caused by the oxidation and rearrangement of cured molecule. These reactions resulted in forming carbonyl and quinone, and leading to a small weight loss by releasing formaldehyde.

From the analysis above, it could be concluded that the curing reaction carried out mainly between 100 and 190 , and the endothermic peaks were useful in explaining the curing behavior.

Analysis of Characteristic Peaks of Curing Behavior

On the whole, the curing process of resole was an exothermic process. However, in 130 to 160 region, there were always one or several sharp endothermic peaks existing, and the related weight loss rates rose abruptly (fig.1). The weight loss in this region was very apparent. Under high-pressure condition, these endothermic peaks would be reduced or disappear [5].

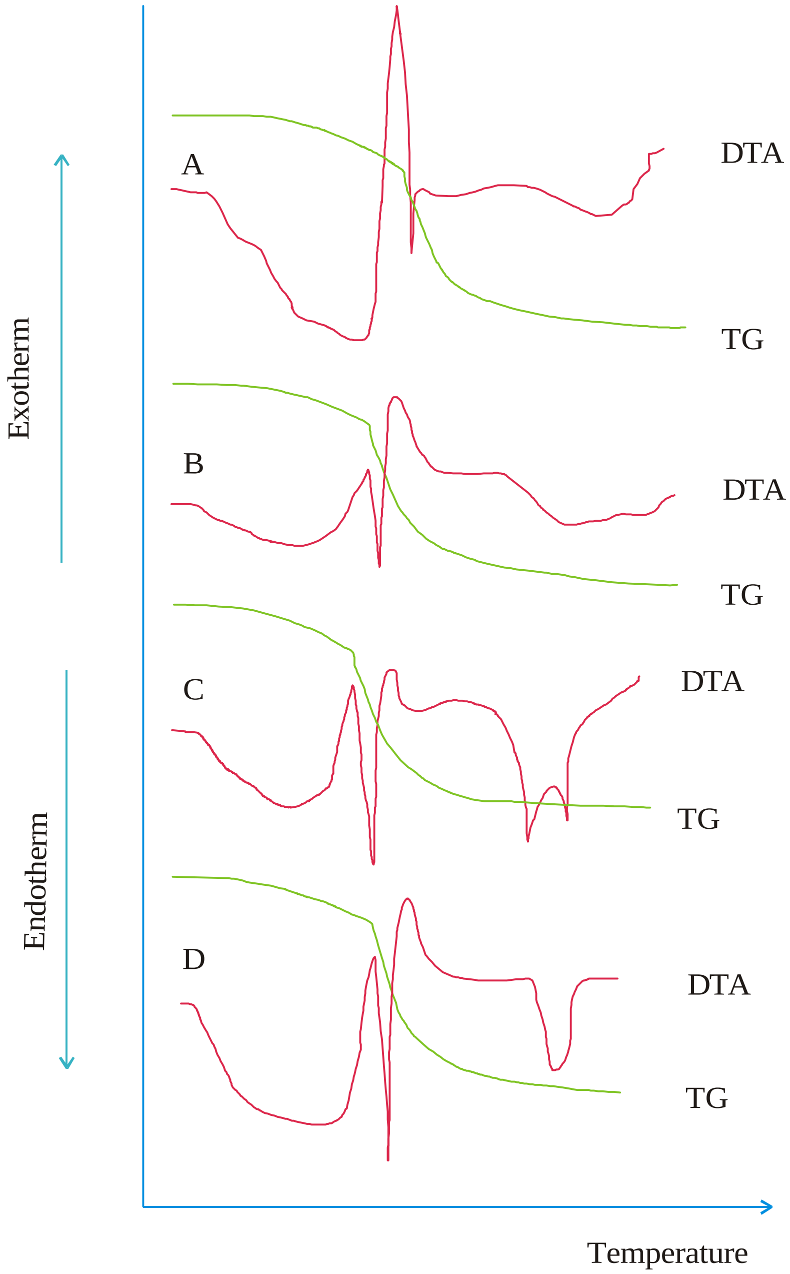
Endothermic peaks between 130 and 160 indicated that lots of condensation by-products were released during this period, and the curing rate was high. Therefore, one or several peaks existing in this area could be used to identify the curing reaction and describe the flowing features of resole. They could be regarded as the characteristic peaks of curing behavior.

Effect of Catalyst on Characteristic Peaks of Curing Behavior

Alkali metal, alkali earth metal oxides and hydroxides could accelerate the curing rate of resole. Curing behavior of resole varies with both the type and amount of curing catalysts added. The effects of different catalysts mainly depended on the ion radius of metals. The larger ion radius of the alkali earth metal hydroxides resulted in a faster curing speed for the resole [6].

After comparison, oxides or hydroxides of Ca and Mg were chosen because they were fitted to technical process rather than the others. They could make the curing rate of resole proper. The DTA and TG thermograms of resole with different amounts of the basic Ca-Mg catalyst was shown in figure 2. Data were presented in Table 1. Apparently, when the resole was curing in the presence of catalysts, decreases in curing temperature and the exothermic final temperature were observed. Meanwhile, the weight loss was increasing.

From the data in the table 1, it could be concluded that the catalyst amount was usually 10% to 15%.



A: without curing catalyst; B: 5% Ca-Mg curing catalyst;
C: 10% Ca-Mg curing catalyst; D: 15% Ca-Mg curing catalyst;

Fig.2: DTA and TG thermograms of resole with different amounts of the basic Ca-Mg catalyst

Table 1: The analysis data of DTA and TG of resole with the change of the basic curing catalyst amount

Catalyst amount (%)	Exothermic peak temperature( )	Endothermic peak temperature( )	Weight loss ratio* in endothermic process (%)
0	92-156-190	134-156	14
5	96-157-194	128-137	45
10	80-158-177	121-134	50
15	73-147-172	127-130	48

*It refers to the ratio in total weight loss during curing process.

Use of Endothermic Peaks in Determining Process Parameters of P-SMC

As characteristic peaks of curing process, the curing endothermic peaks of resole are of great use. It could be used to determine various phenolic composite process parameters. In study of the curing process of P-SMC by DTA and TG (as fig.3), the thickening (the curve of resole viscosity to thickening time was shown in as fig.4) made the temperatures of endothermic and exothermic peaks decreased (as table 2), which were similar to the actual molding process. The relation of the Barcol hardness of products to the actual molding temperature was shown in fig.5. The molding temperature could be determined according to the temperatures of characteristic peaks, usually 20~30 higher than the characteristic endothermic temperature. The curing by-products should be emitted when the temperature of the molding material was around the temperature of the characteristic peaks.

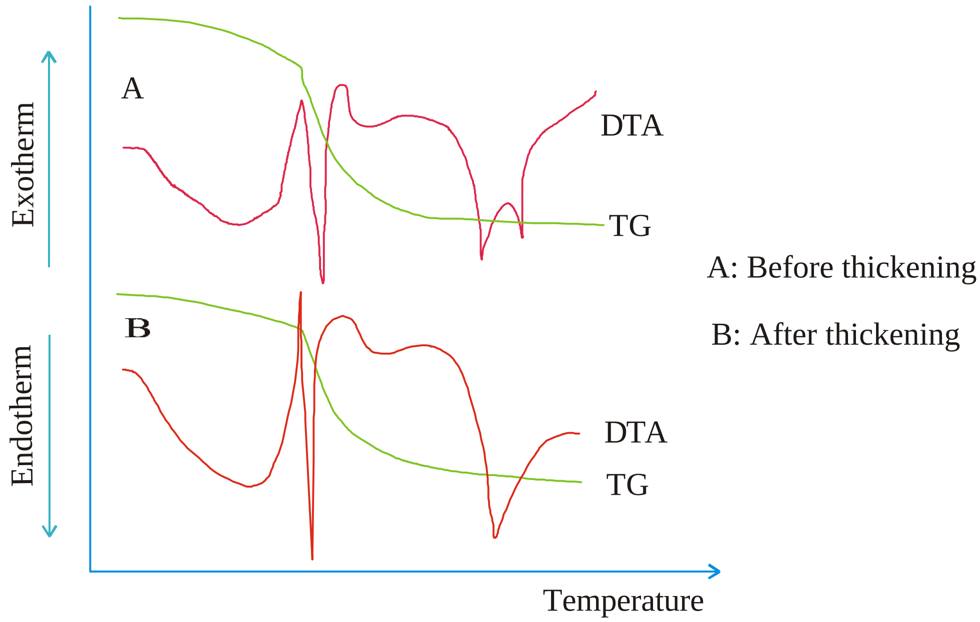
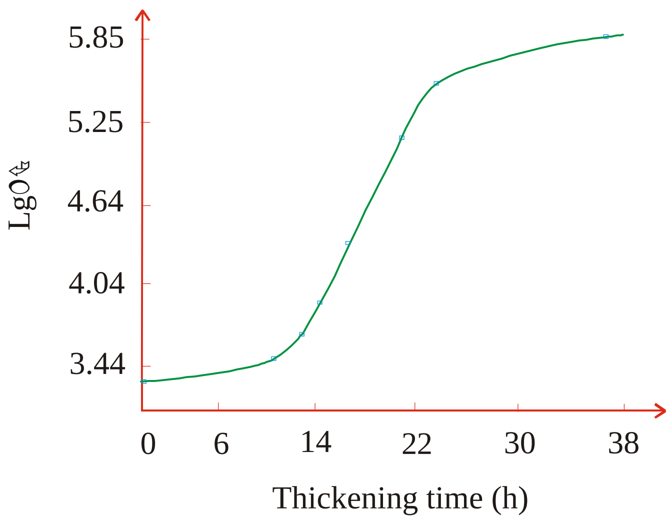


Fig.3: DTA and TG thermograms of P-SMC before/after thickening



* The amount of basic curing catalyst was 10%.

Fig.4: The curve of resole viscosity to thickening time

Table 2: The analysis data comparisons of DTA and TG before/after thickening of resole SMC

	Exothermic peak Temperature( )	Endothermic peak temperature( )	Weight loss ratio* in endothermic process (%)
Before thickening	80-158-177	134	7.4
After thickening**	88-145-172	125	6.4

* It refers to the ratio in total weight loss during curing process.
** 24h for thickening; The amount of basic curing catalyst is 10%.

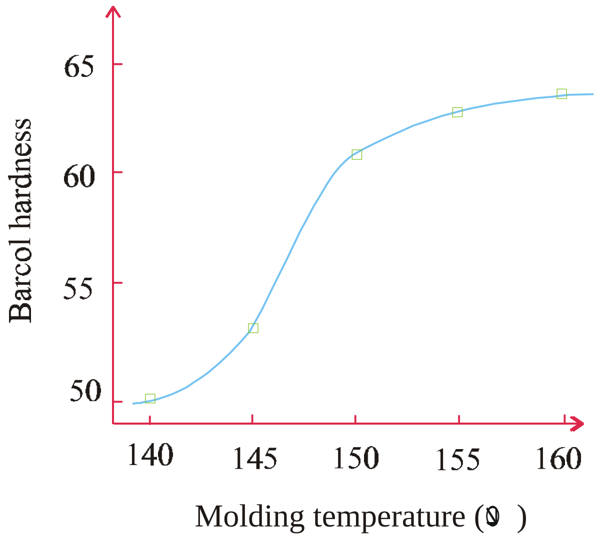


Fig.5: The relation of Barcol hardness to the molding temperature

CONCLUSION

The characteristic endothermic peaks of resole curing behavior could be used to identify the curing reaction and flowing feature. They were about in 135 to 155 , and decreased with increasing of the amount of basic Ca-Mg catalysts. They were important and useful in determining the process parameters under high temperature. As to SMC, the molding temperature was 20~30 above the characteristic endothermic temperature.

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