

Property Study of the Modified Epoxy-Bismaleimide – TOA System

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Synopsis

The Epoxy-Bismaleimide-TOA system is modified by a reactive oligomer made by ourselves with the catalysis of lead carboxylate. The modified system exhibits long storage life (more than 4 months) at room temperature due to its relatively high curing reaction apparent activation energy ($E_a > 70 \text{ kJ/mol}$). The cured system remains good dielectric properties either at room temperature or at 155°C . In addition, the impact strength is up to 13.6 kJ/m^2 at room temperature, the static flexural strength arrives to 13.0 Mpa at 155°C . Moreover, within the range from room temperature to 200°C , the dynamic mechanical modulus is greater than 100 Mpa , and the thermostable index is high (above 155°C) enough to meet the F-class requirement for the electrical insulating materials. The modified system is very suitable to be applied to preparing the binders for F-class micropaper tapes.

Introduction

The binders for F-class rich micropaper tapes nowadays used in giant high pressure electrical machinery in our country are mainly the Epoxy-Bismaleimide-TOA system and the Epoxy-TM (tung oil anhydride bismaleimide co-oligomer) system. Both of them are identical in nature^[1].

The micropaper tapes prepared by the binders have lower flexural strength at high temperature and impact strength at room temperature in comparison with international advanced level. In order to get improved, the systems should be modified by incorporating some other components to increase appropriately their intercrosslinking density. During the study and preparation, there have been considerable efforts in the search for effective modifiers and suitable procedure for improving the properties of the system. Finally, the modifiers and the corresponding procedure have been found. The testing results reveal that for the new cured system, the flexural strength at high temperature and impact strength at room temperature are greatly improved, meanwhile, the dielectric properties and the thermostability are still excellent. The binder of modified system has good storage property.

Experimental

The Binder YXH-Ia was prepared by the reactions between Epoxy 618, TOA, Modifiers and accelerators under certain conditions. The bars and the plates for the testing of the electrical properties and the mechanical properties were made on a given condition: $130^\circ\text{C} \rightarrow 180^\circ\text{C}/6\text{h}$. The filings for the determining of the thermostability were obtained from the bars with a clean smooth file, and they were devolatilized in an electric oven at 180°C for 8h.

Results and Discussion

1 Curing Reaction Kinetics

The two methods to get the activation energy of the curing reactions are as followed:

(a) DSC (Differential Scanning Calorimetry) method

The thermal curing experiments were carried out at some certain heating rates in a differential scanning calorimeter. The thermopositive peak temperature T_p is the function of heating rate V because the reaction degree is a constant. The function is given as^[2]

$$\ln V = -1.052Ea/RT_p + C \quad (1)$$

V : heating rate, K/s; Ea : apparent activation energy, J/mol; R : gas constant, J/(mol.K); T_p : thermopositive peak temperature, K; C : a constant.

The experimental data can be plotted as $\ln V$ versus $1/T_p$, shown in Fig. 1. The plot gives a decent straight line, and the apparent activation energy can be easily calculated from the slope k_{slope} of the straight line. Meanwhile, Arrhenius frequency factor A and rate constant k can be obtained from Kissinger formula^[3]

$$A = VEa/RT_p \exp(Ea/RT_p) \quad (2)$$

$$k = A \exp(-Ea/RT_p) \quad (3)$$

The experimental and calculated results are listed in Table 1.

Table 1 DSC experimental and calculated results

| V [°C/min] | T_p [°C] | CRTR* [°C] | CRT** [min] | ΔH *** [J/g] | Ea [kJ/g] | $\ln A$ [A: min ⁻¹] | k [min ⁻¹] |
|-----------------|------------|------------|----------------|-------------------------|-------------|------------------------------------|--------------------------|
| 5 | 205 | 143-295 | 30 | 343 | 71.1 | 16.22 | 0.817 |
| 10 | 223 | 150-295 | 14.5 | 348 | 71.1 | 16.19 | 0.348 |
| 20 | 243 | 122-320 | 9.9 | 350 | 71.1 | 16.14 | 0.643 |

CRTR: Curing Reactions Temperature Range;

CRT: Curing Reaction Time;

ΔH : Enthalpy changes of curing reactions.

Seen from the Table 1, every peak point temperature T_p increases with the heating rate V . The thermal effect of curing reaction, ΔH , is the function of V , and the curing reaction time decreases with the highening of V .

(b) Gelation time method

According to Flory Gelation Theory, the reaction degree is a certain constant when polymerization reaches gelling point. The experimental data can be depicted as $\lg t_{\text{gel}}$ versus $1/T$ (t_{gel} is gelation time, s; T is reaction temperature in K), shown in Fig. 2. The figure gives a decent straight line. The apparent activation energy Ea of the cured system can be worked out from the slope k_{slope} according to the following

formula:

$$E_a = 2.303R k_{\text{slope}} \quad (4)$$

The calculated result of E_a is 73.4kJ/mol. By comparison, the data of E_a from two methods are almost identical. Moreover, the higher E_a is, the more the reaction rate depends on its temperature, as we know. The Binder YXH-Ia has higher curing rate at higher temperature and has lower curing reaction rate at lower temperature because of its higher E_a . Therefore, the system will be cured quickly at high temperature but has long storage life at room temperature.

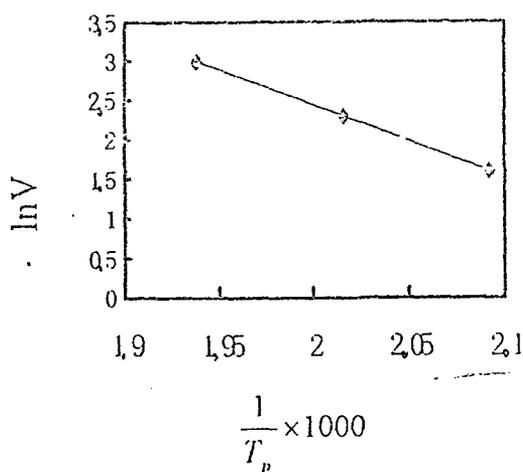


Fig.1. $\ln V [V: ^\circ\text{C}/\text{min}]$ versus $1/T_p [T_p: \text{K}]$

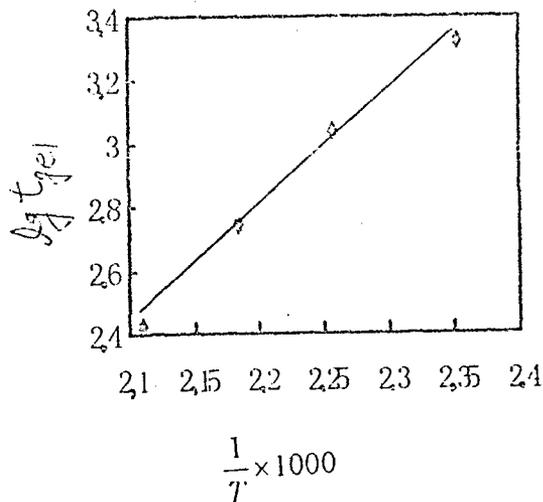


Fig.2 $\lg t_{\text{gel}} [t_{\text{gel}}: \text{s}]$ versus $1/T [T: \text{K}]$

2 Storage life

The products' quality and use life are directly affected by the stability of the binder. Binder YXH-Ia was solvated in some test-tubes with quantitative mixed solvents, and kept for four months at room temperature (23°C), and there were no precipitate to be discovered and the solution remained transparent and clear. The storage life of micapaper tapes depends on that of their binders, so it can be obtained by determining periodically gelation time of their binders (no solvents) at a regular temperature. Gelation time of Binder YXH-Ia was determined and listed in Table 2.

Seen from the Table 2, the gelation time has not decreased remarkably within four months, that is to say, the Binder YXH-Ia has long storage life, which is consistent with its higher apparent activation energy.

Table 2. Gelation time of Binder YXH-Ia (170°C)

| Date | I | II |
|---------|------------|-----------|
| Feb. 14 | 16min40sec | 8min20sec |
| Feb. 24 | 15min11sec | 8min50sec |
| Mar. 07 | 14min02sec | 8min29sec |
| Apr. 22 | 13min07sec | 9min32sec |
| May 16 | 11min53sec | 9min41sec |
| June 18 | 11min02sec | 7min07sec |

3 Mechanical properties

The static flexural strength SFS (at 155°C) and the impact strength IMS (at 25°C) were determined and shown in Table 3.

Table 3 The results of static flexural strength (155°C) and impact strength (25°C)

| Samples | SFS [MPa] | IMS [kJ/m ²] | S* |
|---------|------------|--------------------------|-----|
| YXH-Ia | 13.0 | 13.6 | 0.5 |
| E*** | Very low** | 9.5 | 2.5 |
| H*** | Very low** | 21.5 | 7.7 |

* S is standard variance of IMS data;

** Sample E and H get softened while they are heated to 100°C;

*** Comparative samples, E is Epoxy-Bismaleimide-TOA cured system; H is Epoxy-TOA cured system

The dynamical mechanical properties were detected and can be found in Fig.3. At the same temperature, the cured system whose dynamic mechanical moduli are higher have lower mechanical relaxation losses. In comparison with the Epoxy- TOA system (Sample H), the Epoxy-Bismaleimide-TOA system (Sample E) has higher moduli at the same temperature. The corresponding glass transition temperature T_g moves about 40°C towards the direction of higher temperature. Seen from above, the rigidity of the cured system is increased and its mechanical properties at high temperature get improved and its mechanical relaxation loss decreases when the structure of bismaleimide is introduced into the Epoxy-TOA system. Moreover, the Epoxy-Bismaleimide-TOA system has the structure of interpenetrating polymer networks (IPN)^[4], which is one of the reason why the mechanical properties get improved. In addition, the peak value of mechanical relaxation loss of Sample YXH-Ia is much lower than those of Sample H and E, and its peak location relatively moves 50-100°C towards the direction of higher temperature. Seen clearly from Table 3, the impact strength of YXH-Ia (25°C) is lower than that of H, but higher than that of E. That is mainly because the structure of bismaleimide and the modifiers were incorporated into Sample YXH-Ia, resulting in the increases of the intercrosslinking density and the rigidity of the molecular chains. However, the dispersion of the impact strength of

YXH-Ia is very narrow. Its standard variance is only about 0.5, but that of Sample H highly reaches 7.7. Therefore, the distribution of the impact strength of Sample YXH-Ia is more focal than that of Sample H, which is beneficial for the stability of the properties of the products.

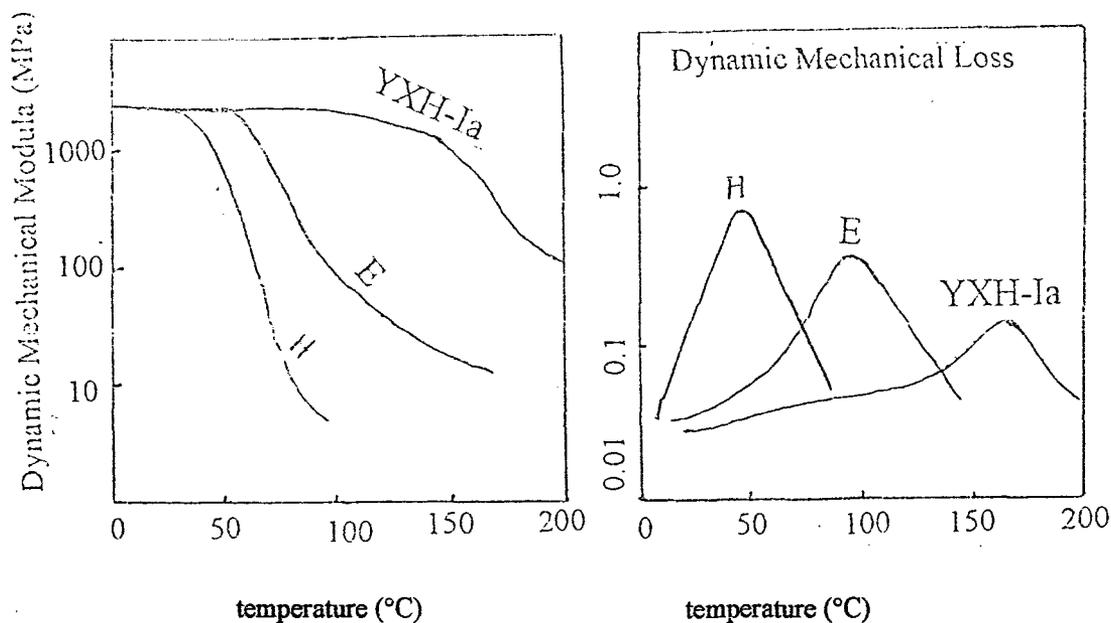


Fig. 3 Dynamic mechanical moduli and mechanical loss change with temperature

4 Dielectric properties

The dielectric dissipation was detected and depicted in Fig.4. The peak value of the dielectric dissipation of the Epoxy-Bismaleimide-TOA system (Sample E) is much smaller than that of the Epoxy-TOA system (Sample H), and the peak location is also higher than that of Sample H. This shows that the Epoxy-TOA system introduced the structure of bismaleimide into is improved to a great extent in dielectric property. On the one hand, the structure of bismaleimide introduced into raise the glass transition temperature of Epoxy-TOA system, and leads the peak to remove to the direction of higher temperature. So the peak location of Sample E is higher about 30-40°C than that of H. On the other hand, the symmetric structure of bismaleimide reduces the polarity of the cured system, lowers the relaxation loss and cuts down the peak value. In one word, Sample YXH-Ia has not only lower dielectric dissipation but also higher peak location, which is very suitable to be applied to preparing F-class binder for rich micropaper tapes.

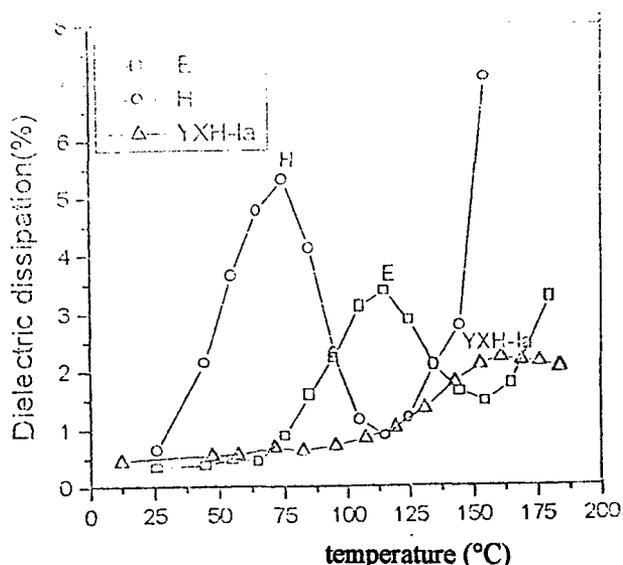


Fig. 4 Dielectric dissipation (%) versus temperature (°C)

5 Thermostability

TG results are listed in Table 4. The thermostable index T_z of the Epoxy-Bismaleimide-TOA system (Sample E) is raised about 2-4°C, the temperature T_B is raised about 10-20°C in comparison with that of the Sample H. So the structure of bismaleimide improves the Epoxy-TOA system in thermostability. The thermostable index T_z and T_B of Sample YXH-Ia are much higher than those of Samples E and H.

The T_z of YXH-Ia is high (above 155°C) enough to fulfil the F-class requirements of the thermostable classes for the electrical insulating materials. Therefore, the modified Epoxy-Bismaleimide-TOA system (Sample YXH-Ia) is improved to a great extent in thermostability.

Table 4 TG results

| | YXH-Ia | E | H |
|------------|--------|-------|-------|
| T_z (°C) | 176.2 | 149.1 | 147.5 |
| T_B (°C) | 532 | 429 | 409 |

T_B : 50% weight loss temperature

Conclusions

The structure of the bismaleimide introduced into the Epoxy-TOA system is beneficial to improve its mechanical properties, dielectric properties and thermostability. The modifiers make the Epoxy-Bismaleimide-TOA system improve in thermostability and mechanical properties to a great extent, meanwhile, the modified system remains excellent dielectric properties. Binder YXH-Ia not only has above-mentioned superior properties but also has long storage life. Binder YXH-Ia is very suitable to be applied to preparing F-class rich micapaper tapes.

References

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