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Curing Behavior of Melamine-Urea-Formaldehyde (MUF) Resin AdhesiveHong Lei^{1*}, Charles E. Frazier²

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Abstract: In this work, MUF resin was tested by DMA method. It showed that G' curves and strain curves together could be used to predict the curing behavior of MUF resins. The study showed that sequential formulation was preferred for the preparation of MUF resins. Hardener could accelerate the curing of MUF resins. But its addition amount should not be too high to affect the resins' shelf time. MUF showed medium thermal resistance when compared with UF and MF resins.

Key words: DMA, curing behavior, MUF resin

1. Introduction

Amino resins are based on the reaction of chemical compounds containing primary or secondary amine groups i.e. -NH_2 or -NH with aldehydes. Three of them, specifically urea-formaldehyde (UF), melamine-formaldehyde (MF) and their co-condensation resin melamine-urea-formaldehyde (MUF), are the main resin adhesives used in the wood industry for the preparation of wood panels. They have dominated the wood adhesive market for a long time and cover at least 60% of the total usage of wood adhesive worldwide. UF resin is the most important adhesive for non-structural wood composites and MF resin for the preparation of impregnated laminated paper for furniture products. The application of MUF resin is similar to the UF resin. However, with higher moisture resistance than UF resin and lower cost than MF, MUF resin is mainly used to produce panels with higher performance, such as for kitchen, floor or some structural composites. Actually, with the decrease of the molar ratio of urea to formaldehyde forced by the more stringent formaldehyde emission regulations, melamine-fortified UF resin or MUF resin with higher percent of melamine are becoming the main application forms rather than pure UF resin in industry to meet with the formaldehyde emission and strength requirements. The study on MUF resins get more and more important.

Curing is the necessary procedure for the formation of bonding strength for wood adhesives. The factors affecting the curing of adhesives include pH, degree of polymerization, catalyst, press procedures, and so on. The study of cure behavior will be helpful for the application of thermosetting wood adhesives. There are many methods to predict the curing behavior of adhesives during curing, such as differential scanning calorimetry (DSC)^[1-3], thermogravimetry – differential thermal analysis (TG-DTA)^[4,5], dynamic mechanical analysis (DMA)^[6-9] and inverse gas chromatography (IGC)^[10-11]. DMA is the most useful method for studying the viscoelastic properties of adhesives. By measuring the storage modulus (G'), the loss modulus (G'') and $\tan \delta$ of samples under a temperature or frequency ramp, the mechanical properties of resins can be predicted and

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valuable information about their curing behavior obtained. The instruments used for dynamic mechanical analysis include dynamic mechanical analyzer, oscillatory rheometer and others. Dynamic mechanical analyzer is the most commonly-used instrument to study the mechanical properties of wood adhesives, such as UF^[12] and MUF^[13-15]. However, the use of oscillation rheometers for assessing the dynamic mechanical characteristics of adhesives has been limited. Kariz *et al* used strain mode to study the effects of heat treatment of wood on the bonding of wood with MUF resins. Wood discs were used in the testing to simulate solvent absorption from the adhesive into the wood during curing. But some problems still exist with this method because of water absorption, non-uniform swelling of the wood in different directions and wood shrinkage due to drying at higher temperatures^[16].

In this work, filter paper was used as substrate for the DMA testing to study the curing behavior of amino resin adhesives. Paper is a good substrate for DMA testing for two reasons: (1) paper has good absorption capability of liquid adhesive, which can reflect the formation of a bond line well; (2) paper will not affect the testing results because of its uniform structure and composition. The aim of this work was to predict the curing behavior of amino resins and optimize the preparation of MUF and other amino resins.

2. Materials and methods

2.1 Materials

The substrate paper was fisherbrand qualitative filter paper, distributed by Fisher Scientific, U.S. It had medium to fine porosity and slow flow rate. Before the preparation of specimens with resin, the paper with thickness ~0.22mm was cut to 5mm wide strips. UF, MF and MUF resin were prepared in the lab. Urea, melamine, $(\text{NH}_4)_2\text{SO}_4$ was chemical grade. 37% aqueous formaldehyde was used in this work.

2.2 Resin preparation

Two kinds of MUF resins, sequential and non-sequential resin, were prepared in this work. In the sequential MUF resin formulation, the addition of melamine and urea were conducted according to their respective reactivities with formaldehyde with a known sequential manufacturing procedure. This was done to ensure the maximum extent of copolymerization of melamine and urea. This type of formulation generally gives very strong bonds. However, in the non-sequential MUF resin, the addition of chemicals followed a pattern apparently diverging from the sequential MUF.

The sequential and non-sequential MUF was prepared based on the methods already reported^[17]. The preparation of sequential MUF with molar ratio $(\text{M}+\text{U})/\text{F}=1.2$ was as follows: To 165 parts of formaldehyde 37% were added 39 parts urea. The pH was set at 10-10.5 and the temperature brought to 92-93 °C under mechanical stirring. The pH was then lowered to 7.8-8.0 by addition of acetic acid 30% solution, and the reaction continued at the same temperature. The pH fell by itself over a period of 1 hour to 1 hour 30 minutes to 5.0-5.3 and then was brought to 9.5 or higher by addition of NaOH 30%. 41 parts of melamine were added to the reaction mixture. When the water tolerance arrived at 200-220%, 6.5 parts of second urea was added and the pH was again brought to 9.5. Then the resin with name of MUF1 was cooled and stored.

The non-sequential MUF adhesive formulation of the same molar ratio $(M+U)/F=1.2$ was prepared as follows: To 569 parts of formaldehyde 37% were added 90 parts urea and the pH of the mixture was adjusted to 9.0 by adding a few drops of 30% NaOH solution. The temperature was brought to 30 °C and then 175 parts of melamine powder was added. The reaction was conducted throughout in a glass reactor equipped with a reflux condenser and always under mechanical stirring. The temperature of the reaction mixture was brought to 94 °C over a period of 1 h with the pH reducing to 8.5. The reaction was kept at 94 °C for 30 min and the pH further decreased to 7.5. The turbidity point, measured at 30 °C, is generally reached at this stage. The pH was adjusted to 9.0 by addition of 30% NaOH solution, and then a second amount of 46 parts of melamine was added to the reaction mixture. A small amount of 30% NaOH solution was added continuously to avoid the pH decreasing too much. The reaction was continued for 15 min and then 155 parts of urea was added. The reaction mixture was kept at 70 °C for 3-5 min and the pH maintained at 9. The reaction mixture was then cooled slowly to reach a temperature of 45 °C after about 1 h cooling. Once the resin had cooled to room temperature, the resin, with the name of MUF2, was stored at pH 8.5-9.0.

The UF resin of total molar ratio $F/U=1.2$ was prepared as follows: 58.2 parts of formaldehyde 37% and 16 parts of urea were added to a 100ml flat bottom flask equipped with a condenser, thermometer and magnetic stirrer bar. The temperature was brought to 70 °C under continuous mechanical stirring of the reaction mixture. The pH was adjusted to 7.2-7.6 by using NaOH 30% solution. The temperature was increased to 90 °C as fast as possible and 6.1 parts of second urea were added. The reaction was maintained for 30 minutes. Then the pH was adjusted to 5.4-5.6 by acetic acid 30% solution. After 60 minutes, the pH was adjusted to 7.5-8.5, and then 13.8 parts of third urea was added. The reaction was continued at 90 °C for 30 minutes. The resin was then cooled to room temperature and stored at pH 8.5-9.0.

The MF resin of total molar ratio $F/M=2.5$ was prepared as follows: 40.54 parts of 37% formaldehyde solution was added to a 100ml flat bottom flask. The pH was adjusted to 9.0-9.5 with NaOH 30% solution. Then 25.2 parts of melamine was charged. During 20 to 30 minutes, the temperature was brought to 85 °C. At 70 °C, the solution became transparent with the pH being maintained above 8.5. The reaction could not be stopped until 500% water tolerance was achieved. The resin was then cooled to room temperature and stored at pH 8.5-9.0.

2.3 DMA test

Specimens for DMA testing were prepared by soaking filter paper strips in resin solution with 2% $(NH_4)_2SO_4$ as hardener on solid resin for 1 minute. $(NH_4)_2SO_4$ was used as a 30% solution. Excess resin was removed to make sure all of the specimens had similar resin loading i.e. about 0.014 ± 0.005 g dry resin per 22mm-long paper. After impregnation, the specimens were left at room temperature for 15 minutes, and then were dried in an air oven at 60°C for 60 minutes to establish a low level of cure and rigidity. After drying, the specimen weight was stable with no residual water. All of the specimens were tested within 6 hours of preparation to avoid the effects of further cure at room temperature on the final results. Specimens left at room temperature for more than 6 hours were

discarded.

Using a TA Instruments AR1000 Rheometer, DMA was conducted in torsion while the specimens were subjected to a 3N tensile force (clamping torque = 20 cN•m). The frequency was fixed at 1 Hz (determined from preliminary frequency sweep experiments as the highest frequency not complicated by clamp inertia effects).

All tests were conducted within the linear viscoelastic response (LVR) region. This was determined from stress sweep experiments at the temperature extremes with unresinated paper specimens and also resinated paper (composite) specimens. The LVR limit was defined as the stress level above which the correlation coefficient of the stress/strain plot (R^2 , the least-squares fit) fell below 0.9995.

Composite specimens were subjected to temperature ramps (25°C – 250°C; 5°C/min; oscillation stress = 5MPa).

Two or three replications were conducted for each sample type.

2.4 TG test

30-40mg UF, MF and MUF resin samples with 2% solid $(\text{NH}_4)_2\text{SO}_4$ as hardener on solid resin was tested by TG instrument. Samples were heated from room temperature to 500 °C at a rate of 10 °C/min in N_2 .

3 Results and discussion

3.1 General curing reaction of MUF resin

Figure 1 shows the temperature ramp for the MUF1 adhesive. The G' curve could be divided into four regions: (1) from room temperature to 92.4 °C: in this region, G' of MUF1 decreased firstly rapidly and then slowly, which could be explained by the softening of partially cured MUF resin; (2) from 92.4 °C to 158.9 °C: in this region, G' increased, which indicated that the curing of the MUF resin outpaced its softening; (3) from 158.9 °C to 185.9 °C: G' got to a relatively stable plateau, which meant that heat had little effect on the stiffness of completely-cured MUF in this region; (4) from 185.9 °C to 220 °C: G' decreased with the increase of temperature, which suggested MUF1's poor thermal resistance in this region. At 92.4°C, not only did G' exhibit a minimum value, a maximum strain was also found. 92.4 °C was the threshold of G' and strain. It marked the onset of the curing of the MUF1 resin and was the curing temperature (T_{cur}) of MUF1. The peak in $\tan \delta$ is normally interpreted as the gelation temperature (T_{gel}) of resins. Here, it was 103.8 °C.

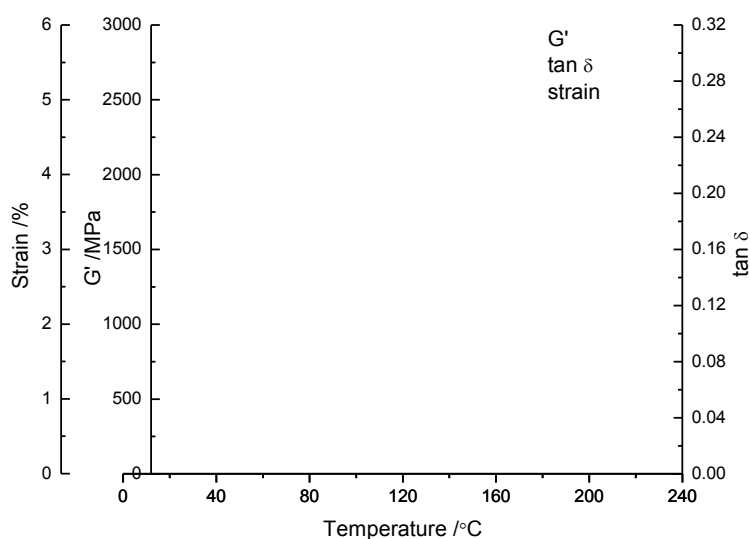


Figure 1. Temperature ramp of MUF1

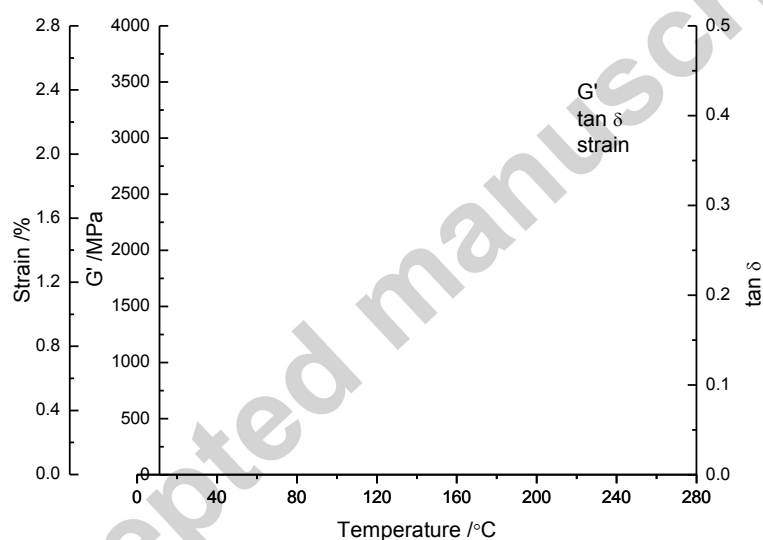


Figure 2. Temperature ramp of MUF2

MUF1 and MUF2 adhesives had similar curing behavior as indicated in Figures 1 and 2. However, for the two formulations, it was obvious that MUF2 cured more slowly than MUF1. T_{cur} of MUF2 was 103.8 °C, at which the maximum strain and minimum G' were found as seen in Figure 2. T_{cur} of MUF2 was 11.4 °C higher than that of MUF1. The T_{gel} of MUF 2, determined from the $\tan \delta$ curve, was 123.6 °C, which was higher than the 103.8 °C for the MUF1 adhesive. Even before the obvious decrease of G' at 197.3 °C, there was no plateau region, which indicated that from 103.8 °C to 197.3 °C, the curing of MUF2 had not stopped. A wide temperature range of curing was further proof of the slow curing of the MUF2 resin. The slow curing speed of MUF2 might be caused by the lower reaction degree before curing. For both MUF formulations, the mass ratio M/U was 47:53. The addition amount of urea was even higher than melamine. Despres *et al* had proved the co-condensation reaction between melamine and urea fractions^[18]. However, even in a

system with higher percent of melamine, the percentage of co-condensate was rather low [19]. The performance of the final resin still depended largely on the performance of the UF and MF resins themselves. Therefore, the reaction degree of urea with formaldehyde would affect the curing of the final resin considerably. It is well-known that the condensation reaction under base condition for the preparation of UF resin is very slow. The resulted UF fractions with lower reaction degree then affected the curing of MUF resin. To increase the curing speed of non-sequential MUF resin, the reaction time before the addition of the second loading of urea might be shorter and the time after the addition of urea might be lengthened. In all, the reaction degree of UF condensate and MF condensate was one of the key factors in the control of the curing speed of MUF resins.

At 197.3 °C, the strain of MUF2 showed an abrupt increase. This could be caused by the decomposition or rips on the surface of the test specimens and will be discussed later. Although for MUF1, G' began to decrease and the strain began to increase from 185.9 °C, the change of strain was not as severe as seen in MUF2. It might suggest the different cured structure of the two MUF resins. In all, the DMA results showed that MUF1 had better thermal resistance and curing performance than MUF2. Sequential formulation was preferred for the preparation of the MUF resin.

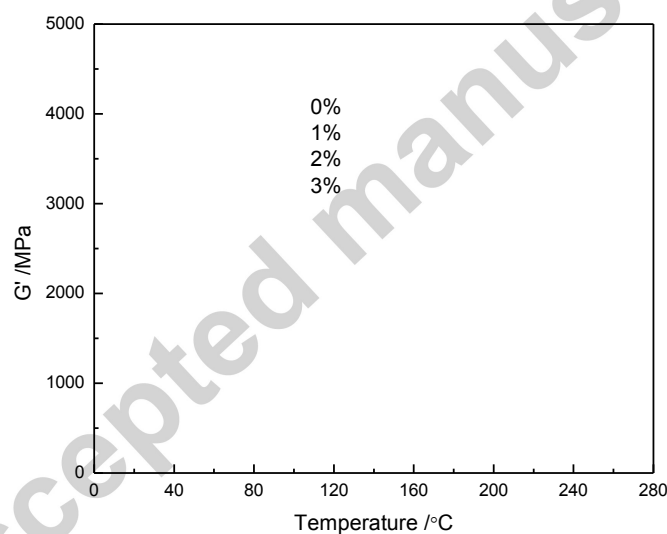


Figure 3. G' curves of MUF1 with different addition amount of hardener

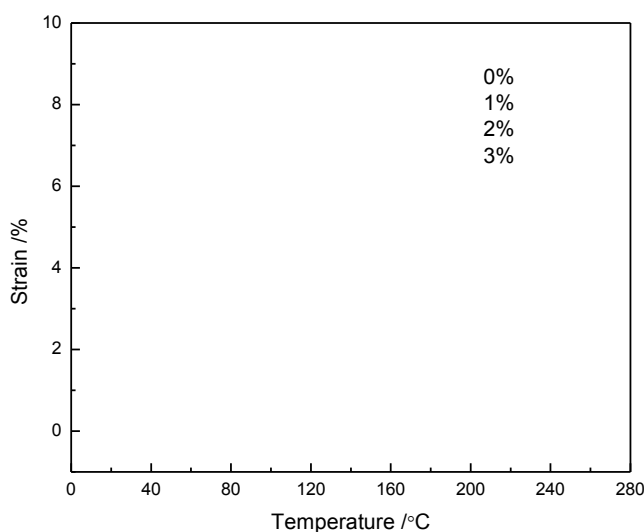


Figure 4. Strain curves of MUF1 with different addition amount of hardener

The effects of hardener concentration on the curing speed of MUF resin can be seen from Figure 3 and Figure 4. From Figure 3, the G' of MUF with or without hardener showed a similar change tendency, firstly a decrease, then an increase and finally a decrease in the temperature span. The curing temperature of MUF resin was respectively 127.5 °C, 92.2 °C, 92.4 °C, 99.7 °C with 0%, 1%, 2%, 3% hardener. Although MUF resin without hardener could cure, which could be seen by the increase of G' from 127.5 °C, it cured at a higher temperature than those MUF resins with hardener. Its curing temperature was almost 30 °C higher than others with hardener. This indicated that hardener exhibited cure acceleration effects and that its use in the current resins was necessary for the application of MUF resin.

Although the MUF resin had similar curing temperatures with 1%, 2% and 3% hardener, curing speed was different. With an increase in hardener concentration, the temperature to achieve maximum G' decreased, which also meant that the time to achieve complete cure was also shortened. The temperature to achieve maximum G' was about 201 °C, 155 °C, 150 °C for resins with 1%, 2% and 3% hardener, respectively. When hardener concentration was increased from 1% to 2%, the acceleration effects of hardener on MUF were obvious. However, the difference in curing speed for resins with 2% and 3% hardener was relatively small, therefore suggesting that hardener concentration should not exceed 2% of the solid resin in this MUF formulation. Once hardener concentration exceeds 2%, the hardener will not accelerate the curing greatly and it might even affect the resin application because of the shortened shelf time.

The effects of hardener concentration on the curing of MUF resins can be seen clearly by the strain curves shown in Figure 4. As indicated, the strain for all samples firstly increased, decreased and then exhibited a plateau as a function of temperature. Once the strain became stable, the resin cured fully. The fully cured temperature of MUF with 0%, 1% and 2% hardener was approximately 162 °C, 144 °C, 130 °C respectively, indicating a shortened curing time with increased concentration of hardener. Although the difference in curing time between resins with 2% and 3% hardener was not clear, as previously

indicated in Figure 3, the strain for resin with 3% hardener was much lower than that of 2%. This indicated that before the DMA test, the resin with 3% hardener had more non-recoverable cured or thermosetting content than that with 2%. Actually, too much pre-curing before hot pressing is undesirable in applications with MUF resin adhesives for the preparation of wood panels. The resin with 0%, 1%, and 2% hardener showed similar strain before curing, suggesting that after the preparation of specimens for the DMA tests, these resins had similar degrees of cure and that the additional amounts of hardener had limited effects on the curing of the MUF resin studied in this work.

It was interesting to see that the MUF resin without hardener showed two peaks in the strain curve, at 106.4 °C and 135 °C. To explain the two peaks, DMA tests were conducted with UF resin and MF resin. Since the DMA specimens of the UF resin without hardener were too soft to show a high probability to be broken, the DMA test was conducted with the UF resin with 2% hardener (see Figure 5). T_{cur} of the UF resin was 88.6 °C, which was a little lower than the T_{cur} of 92.4 °C for the MUF resin. The UF resin completed curing at about 125 °C, which was almost 30 °C lower than that of MUF. The latter cured completely at about 158 °C. The faster curing speed of the UF resin could be seen by its much lower strain than the MUF resin. Therefore, the press temperature should be higher or the press time longer for the preparation of wood panels when using MUF resin as adhesives in comparison to the UF resin, which is the current approach in industry. The UF resin showed poor thermal resistance as indicated by the decrease of G' and increase of strain at temperatures as low as 132 °C, at which the MF resin almost completed its curing (see Figure 6). The increase of strain at 132 °C explained well the appearance of the second peak in the strain curve of the MUF resin without hardener. Once the MF fractions were completely cured, the strain began to decrease. The temperature at which complete cure of the MF system was observed (132°C) was shown to coincide with the second peak found in the strain curve of the MUF resin in the absence of hardener.

It is important to note that the strain level for the pure UF resin increased substantially at temperatures in excess of 132°C, this being particularly so as temperature approached 150°C. While in Figure 4 for the MUF resin, the increase of strain after curing occurred only after the temperature exceeded 200 °C, it indicated that the MF fraction improved the flexibility of the final MUF resin, which enabled the specimens of the MUF resin withstand the temperature and oscillation stress for a longer time. The TG analysis of the UF, MF and MUF systems indicated that the increase of strain after curing did not result from the decomposition of the resins (see Figure 7). The decomposition temperature was higher than 200 °C for all three resins. For the data in Figure 5, the specimens were not broken completely even after 150 °C when considering the gradually decrease of G' data. The increase of the strain might be caused by the rips of specimens.

With all three systems, the MF resin exhibited the best thermal resistance characteristics, with the UF system showing worst behavior, as indicated in Figures 3, 5 and 6. For MF, there was no obvious decrease of G' being seen after curing in the testing temperature span. Their decomposition temperature seen in Figure 7 showed the same tendency as the thermal resistance. The decomposition temperature for UF, MF and MUF resin was 269 °C, 286 °C, 418 °C, respectively, determined by the peaks of derivative of weight percentage in Figure 7.

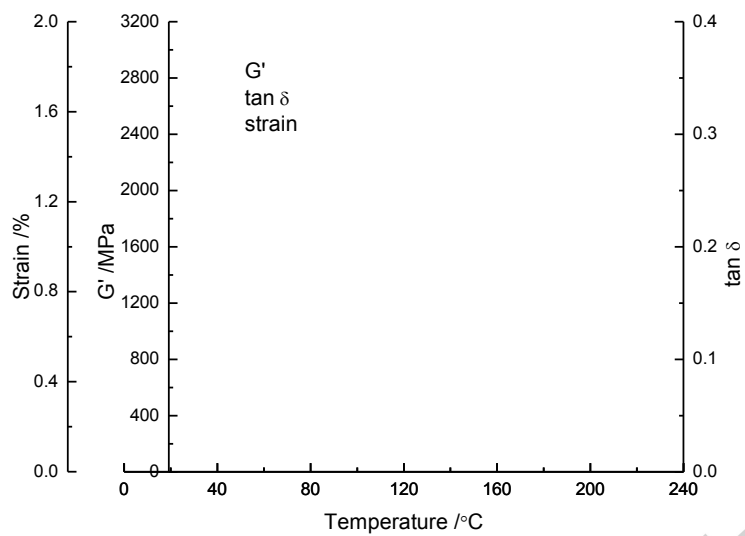


Figure 5. Temperature ramp of UF resin

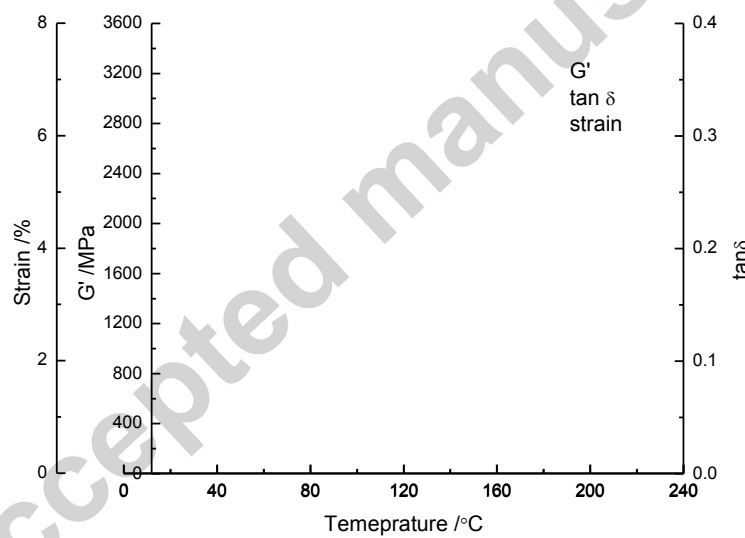


Figure 6. Temperature ramp of MF resin without hardener

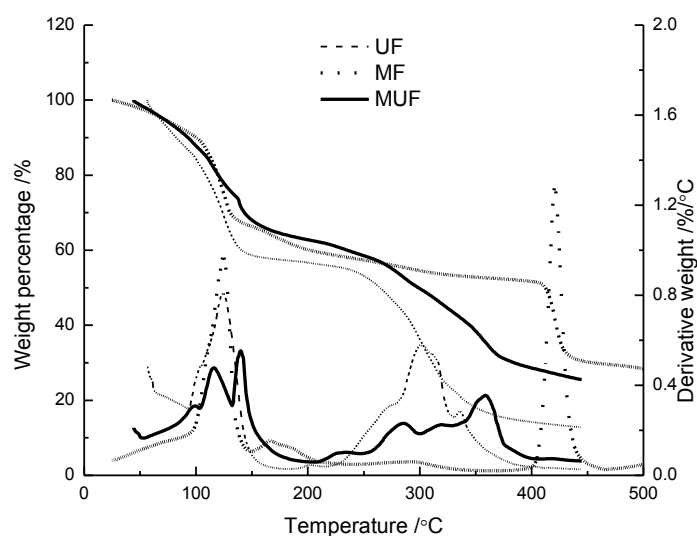


Figure 7. TG of UF, MF and MUF resins

4 Conclusions

In this work, MUF resin was tested by DMA method. It showed that G' curves and strain curves together could reflect the curing behavior. The results were proved with each other. By the study on two kinds of MUF formulations and effects of hardener, some conclusions could be gotten:

- (1) Sequential formulation was preferred for the preparation of MUF resins.
- (2) Hardener could accelerate the curing of MUF resins. But its addition amount should not be too high to affect the resins' shelf time.
- (3) MUF showed medium thermal resistance when comparing with UF and MF resins.

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