Study on Process Optimization and Performance of Low Formaldehyde Etherified 2D Resin

Ma Liu¹*

¹Shandong Vocational College of Science and Technology, Weifang, 261053, China

*E-mail: maliu1215@163.com

Abstract. With the improvement of people's awareness of environmental protection and safety, formaldehyde emission from textiles is strictly restricted in many countries in the world. In this thesis, 2D resin was modified to prepare etherified 2D resin by a one-step process which is simple, time-saving, energy-saving, and quick reaction. The etherified 2D resin has low formaldehyde content, good handle and wrinkle resistance, and its comprehensive properties are superior to those of 2D resin.

1. Introduction

1.1. 2D resin and 2D etherified resin

Dihydroxymethyl diethyl urea termed as DMDHEU, known as 2D resin in China, multi-reactive resin[1-2]. It has excellent washing property and hydrolysis resistance, good storage stability, and is recognized as the best durable pressing finishing agent with anti-wrinkle effect in the market. However, 2D resin has some problems such as formaldehyde release and fabric strength decrease. With the improvement of people's awareness of environmental protection and safety, the amount of formaldehyde released from textiles has been strictly restricted in the world, and the corresponding laws and regulations have been formulated. At present, the etherification of 2D resin is an important way to reduce the formaldehyde content on finished fabrics, whether from the perspective of international market competition, environmental performance, or from the perspective of cost. The comprehensive performance of modified 2D resin is better than that of 2D resin finishing agent with low formaldehyde release, good feeling and anti-wrinkle after modified[3].

Synthesis of 2D resin is the basis of producing etherified 2D resin. There are two kinds of 2D resin synthesis process routes: In the two-step process, urea was cycled with glyoxal to form 4, 5-dihydroxy vinyl urea (DHEU) and then reacted with formaldehyde by hydroxymethyl; The one-step process is that glyoxal, urea and formaldehyde are added into the reactor at the same time, and cyclization and hydroxymethylation are carried out simultaneously. In comparison, the two-step process is more complex and the reaction time is longer. One-step process is simple and the reaction efficiency is faster[4-5].

In this paper, 2D resin was synthesized by one-step process, the synthesis and etherification modification process were optimized, and the application properties of the modified 2D resin were studied.

1.2. Synthesis mechanism

1.2.1. Synthesis mechanism of 2D resins. 2D resin is made from glyoxal, urea and formaldehyde through specific reaction conditions. The reaction process can be divided into two stages. The first
stage is cyclezation stage, that is, the cyclezation reaction of glyoxal and urea generates the primary condensed DHEU. The reaction process is showed in Figure 1.

The second stage is the hydroxymethylation stage, that is, the generated initial shrinkage of DHEU is condensed with formaldehyde to form 2D resin. The reaction process is showed in Figure 2.

1.2.2 Etherification mechanism of 2D resins. The 2D resin was modified by etherification. Ether reagent: methanol and a variety of alcohols etc. The reaction process is showed in Figure 3.

2. Experiment content

2.1. Experimental drugs and materials
Glyoxal (40%, AR, Weifang Risheng Trade Co., Ltd), formaldehyde (37%, AR, Weifang Risheng Trade Co., Ltd), urea (AR, Weifang Risheng Trade Co., Ltd), sodium hydroxide (AR, Weifang Risheng Trade Co., Ltd), hydrochloric acid (Tech technical grade, Weifang Zhongke Medical Equipment Co., Ltd), anhydrous sodium sulfite (AR, Weifang Zhongke Medical Equipment Co., Ltd), resin catalyst NKC (Tech technical grade, Weifang Zhongke Medical Equipment Co., Ltd), resin ELF (Tech technical grade, Weifang Zhongke Medical Equipment Co., Ltd).
White fabric 1: cotton 130×80 50s×40s, white fabric 2: cotton 160×72 40s×80 /2, green fabric 3: cotton 114×70 40s×30s.

Figure 1. Cyclization reaction mechanism.

Figure 2. Mechanism of hydroxymethylation reaction.

Figure 3. Etherification modification of 2D resin.

Figure 4. Etherification modification of 2D resin.
2.2. Experimental Instruments
DF-101S heat-collecting thermostatic heating magnetic stirrers (Weifang Risheng Trade Co., Ltd), CARY 50 UV/visible spectrophotometer (Shandong Yupu Experimental Instrument Co., Ltd), KW-1000DA thermostatic water bath (Weifang Risheng Trade Co., Ltd), EL-A pneumatic electric truck (Weifang Risheng Trade Co., Ltd), MD-3 fabric setting dryer (Wenzhou Fangyuan Instrument Co., Ltd), YG(B)026E electronic fabric strength tester (Wenzhou Fangyuan Instrument Co., Ltd), YG(B)541D fabric crease elastometer (Wenzhou Fangyuan Instrument Co., Ltd), four flask, thermometer, JA2003MAX200 electronic balance(Weifang Risheng Trade Co., Ltd), PHS-3B precision pH meter(Weifang Risheng Trade Co., Ltd), etc.

2.3. 2D resin synthesis process
The formaldehyde and glyoxal were added into flask and were evenly stirred. Further, 20% sodium hydroxide solution was added in order to maintain pH value in the range 6 – 6.5 and simultaneously urea was added, and the solution was heated, and the temperature was maintained at 60°C for 4 hours. 2D resin was obtained by vacuum distillation at 50°C.

2.4. 2D resin etherification process
Methanol was added to the 2D resin at 50°C for 3 hours, pH was adjusted to 1.5-2.0 (50% sulfuric acid). Reduce the temperature to 40°C and adjust the pH value to 4-5 (20% sodium hydroxide solution) to obtain etherified 2D resin.

2.5. Resin finishing process
Two dipping and two rolling (rolling rate 80%) → drying (110°C×1min) → baking (150°C×3min, resin dosage 80-100g/L, resin catalyst NKC 24-30g/L).

2.6. Test method[6]
The content of free formaldehyde in textiles shall be measured in accordance with GB/T 2912.1-2009-textiles- Part 1: Determination of free and hydrolyzed formaldehyde (water extraction method);
Tearing strength of fabric was measured according to ASTM D5034-2009(R2017) Standard Test Method for Tearing Strength and Elongation of Textiles (Grinding Method);
Fabrics crease recovery Angle was measured according to GB/T 3819-1997 Textile fabrics-Determination of crease recovery Angle method;
Fabric no-iron test was graded according to AATCC 124-2010 Smoothness Appearing of Fabrics After Repeated Home Laundering.

3. Results and Discussion

3.1. Optimization of 2D resin synthesis process
The factors that affect the synthesis of 2D resin include: molar ratio, pH value, temperature and time. Taking the content of free formaldehyde in the resin and the wrinkle recovery angle of the textiles as evaluation indicators, single factor analysis of the factors affecting 2D resin synthesis is carried out to determine the best process for 2D resin synthesis.

3.1.1. Mass ratio of glyoxal, urea and formaldehyde. It can be found from the synthesis reaction equation that the 2D resin is the initial condensed body of 1mol urea, 1mol glyoxal and 2 mol formaldehyde. As can be seen from Table 1, when the mass ratio of glyoxal, urea and formaldehyde is 1:1:1.6, although the amount of free formaldehyde is the lowest, the crease recovery Angle of the finished fabric is also the lowest, and the anti-crease effect is poor. With the increase of urea dosage, both free formaldehyde and fabric crease recovery Angle increased. When the molar ratio of substance was 1:1:1.8, the fabric crease recovery Angle reached the maximum value, and the resin free formaldehyde content was only 0.47%. Considering comprehensively, it is determined that the ratio of urea-formaldehyde substances in the synthesis of 2D resin is 1:1:1.8.


Table 1. Effect of molar ratio of substance on synthesis of 2D resin

| N (glyoxal) : N (formaldehyde) : N (urea) | free-formaldehyde release /% | wrinkle recovery angle / (°) |
|----------------------------------------|-------------------------------|-----------------------------|
| 1:1:1.6                                 | 0.35                          | 198.2                       |
| 1:1:1.7                                 | 0.42                          | 223.1                       |
| 1:1:1.8                                 | 0.47                          | 258.9                       |
| 1:1:1.9                                 | 0.58                          | 250.3                       |
| 1:1:2.0                                 | 0.84                          | 255.6                       |

Note: PH6.0-6.5, temperature 60℃, time 4h

3.1.2 pH. Weak acidic conditions are conducive to the whole reaction. However, if the acidity is too high, DHEU will have a side reaction to produce by-product hydantoin. If the reaction is carried out under alkaline conditions, glyoxal is prone to Carnicaro reaction, disproportionation into sodium glycolic acid, the above side reactions are adverse to the main reaction, the resin conversion rate will be greatly reduced, while the quality of the resin is affected. Excessive acidity of DHEU will result in side reaction, resulting in byproduct acetonylurea:

\[
\text{OHC-CHO + NaOH} \rightarrow \text{HOCH}_2\text{-COONa}
\]

As can be seen from Table 2, the pH value of the reaction was 6.0-6.5.

Table 2. Influence of pH value on 2D resin synthesis.

| pH  | 5.5-6.0 | 6.0-6.5 | 6.5-7.0 | 7.0-7.5 | 7.5-8.0 |
|-----|---------|---------|---------|---------|---------|
| free-formaldehyde release /% | 0.54   | 0.47   | 0.5     | 0.56    | 0.63    |
| wrinkle recovery angle / (°) | 247.3  | 254.3  | 245.4   | 238.7   | 230.1   |

Note: N (glyoxal) : N (formaldehyde) : N (urea)=1:1:1.8, temperature 60℃, time 4h

3.1.3 Reaction temperature. Because hydroxymethylation reaction is reversible. The lower reaction temperature, the slower chemical reaction rate and takes a long time to reach equilibrium. Because the boiling point of formaldehyde is -19℃ and the reaction temperature is 70℃, formaldehyde is easy to volatilize, which is not conducive to the synthesis reaction. The return flow during synthesis is significantly increased, resulting in a higher amount of free formaldehyde and a lower wrinkle recovery Angle of the finished fabric. As can be seen from Table 3, when the temperature is 60℃, the free formaldehyde is lower and the crease recovery angle is higher.

Table 3. Influence of temperature on synthesis of 2D resin.

| Temperature/℃ | free-formaldehyde release /% | wrinkle recovery angle / (°) |
|---------------|------------------------------|-----------------------------|
| 50            | 0.61                         | 238.2                       |
| 55            | 0.53                         | 250.5                       |
| 60            | 0.47                         | 251.4                       |
| 65            | 0.58                         | 246.3                       |
| 70            | 0.74                         | 240.6                       |

Note: N (glyoxal) : N (formaldehyde) : N (urea)=1:1:1.8, pH6.0-6.5, time 4h
3.1.4 Reaction time. Keep N (glyoxal) : N (formaldehyde) : N (urea)=1:1:1.8, pH 6.0-6.5, reaction temperature 60℃. Hydroxymethylation reaction is reversible, which need a certain time to reach chemical equilibrium. If the time is too short, the reaction is not complete; If the time is too long, on the one hand, formaldehyde reacts with urea and glyoxal to form 2D resin, and the formaldehyde decreases continuously because it participates in the reaction. On the other hand, the 2D resin generated at the same time dissociates increases the content of free formaldehyde in the solution. When the amount of formaldehyde consumed by synthesis is equal to the amount of formaldehyde produced by dissociation, the reaction reaches a dynamic equilibrium state. As can be seen from the curves of free formaldehyde content measured under different reaction times in Figure 5, the amount of free formaldehyde no longer decreases after 4h of reaction, indicating that the reaction has reached an equilibrium state. Therefore, the appropriate reaction time is about 4 h.

In summary, the optimal process of 2D resin one-step synthesis is N (glyoxal) : N (formaldehyde) : N (urea) =1:1:1.8, pH 6.0-6.5, temperature 60℃, time 4h, and the content of free formaldehyde of the synthesized resin is less than 0.5%.

3.2. Optimization of 2D resin etherification process
The factors influencing the modification of 2D resin include the amount of methanol, temperature, time and pH value. Taking the content of free formaldehyde in the resin and the crease recovery Angle of the fabric as evaluation indexes to analyze the factors that influencing the modification of 2D resin so as to determine the optimal conditions for the modification of 2D resin.

3.2.1. Methanol dosage. As can be seen from Table 4, with the increase of the amount of methanol, the amount of free formaldehyde decreases continuously and the wrinkle recovery Angle becomes smaller. As the amount of methanol increases, under the same amount of resin, the effective amount of 2D resin acting on cellulose fiber decreases, the covalent cross-linking degree decreases, and the cross-linking activity between etherified resin and fiber decreases, so the wrinkle recovery Angle decreases[8-9]. To sum up, the methanol dosage (relative to the 2D resin dosage) of 35% was selected, and the free formaldehyde in the etherified resin was lower, and the wrinkle recovery Angle was higher.

Table 4. Influence of methanol dosage on 2D resin etherification.

| Methanol (Relative 2D resin)/% | free-formaldehyde release /% | wrinkle recovery angle / (°) |
|-----------------------------|-------------------------------|----------------------------|
| 25                          | 0.33                          | 270.7                      |
| 30                          | 0.26                          | 265.8                      |
| 35                          | 0.23                          | 261.5                      |
| 40                          | 0.22                          | 254.6                      |
| 45                          | 0.20                          | 245.6                      |
3.2.2. Influence of pH value. As can be seen from Table 5. The amount of free formaldehyde reduces gradually as the pH value decreases, which means that low pH value was conducive to the resin etherification modification. When the pH value was 1.0-1.5, the wrinkle recovery Angle decreased, but the amount of free formaldehyde increased, which may be caused by the hydrolysis reaction of 2D resin to generate HCHO. The pH value is too high, the etherification reaction is not sufficient, and the content of free formaldehyde in the resin is high. Considering comprehensively, the pH value of etherification is 1.5-2.0, and the etherification reaction is more sufficient.

Table 5. Influence of pH value on 2D resin etherification.

| pH      | free-formaldehyde release /% | wrinkle recovery angle / (°) |
|---------|------------------------------|-----------------------------|
| 1.0～1.5| 0.32                         | 257.6                       |
| 1.5～2.0| 0.23                         | 262.5                       |
| 2.0～2.5| 0.35                         | 266.6                       |
| 3.0～3.5| 0.40                         | 267.4                       |

Note: change pH value, methanol dosage (relative to 2D resin) 35%, etherification temperature 50℃, etherification time 3h

3.2.3. Influence of temperature. Data in Table 6 showed that with the increase of temperature, the content of resin free formaldehyde first decreased and then increased. Analysis reasons: the increase of temperature is conducive to the forward etherification reaction, but due to the low boiling point of methanol (64.7℃), too high reaction temperature is not conducive to the cross-linking reaction between methanol and 2D resin. At the same time, with the increase of temperature, the cross-linking reaction may occur between the resins, and the fold recovery Angle will decrease slightly. Considering comprehensively, the reactivity of methanol is better at 50℃.

Table 6. Influence of temperature on the etherification of 2D resin.

| temperature/℃ | free-formaldehyde release /% | wrinkle recovery angle / (°) |
|---------------|------------------------------|-----------------------------|
| 40            | 0.39                         | 253.6                       |
| 45            | 0.32                         | 263.6                       |
| 50            | 0.23                         | 262.5                       |
| 55            | 0.31                         | 259.7                       |
| 60            | 0.36                         | 256.8                       |

Note: Change the etherification temperature, methanol dosage (relative to 2D resin) 35%, pH1.5-2.0, etherification time 3h

3.2.4. Influence of reaction time. It takes a certain time for the chemical reaction to reach basic equilibrium. As can be seen from the data of free formaldehyde in Table 7, after 4 hours of reaction, the amount of free formaldehyde reaches the lowest value. If the time is extended, the free formaldehyde content will basically no longer decrease, and it may occur between the resins. Cross-linking reaction, the wrinkle recovery angle is slightly reduced. Therefore, the etherification time is 4h.

In conclusion, the optimal process of 2D resin etherification modification is as follows: methanol dosage (relative to 2D resin dosage) 35%, temperature 50℃, time 3h, pH value 1.5～2.0, and free formaldehyde content of the resin after etherification is less than 0.2%.
Table 7. Influence of time 2D resin etherification.

| time /h | free-formaldehyde release /% | wrinkle recovery angle / (°) |
|---------|-------------------------------|-----------------------------|
| 1       | 0.49                          | 263.0                       |
| 2       | 0.39                          | 264.4                       |
| 3       | 0.23                          | 262.5                       |
| 4       | 0.23                          | 260.9                       |
| 5       | 0.24                          | 257.7                       |

Note: Change the etherification time, methanol dosage (relative to 2D resin) 35%, pH value 1.5-2.0, reaction temperature 50℃

3.3. Application comparison of etherified 2D resin CR-E and ELF resin (commercially available)

By comparing and testing the prepared etherified 2D resin CR-E with the commercially available ELF resin finishing agent, the main indexes include fabric breaking strength, tearing strength, formaldehyde content, whiteness, hand feel and iron-free property, and the application performance of the prepared etherified 2D resin was comprehensively evaluated.

3.3.1. Impact on strength. According to the comparative analysis of the data in Table 8 and Table 9, the etherification modified 2D resin CR-E treatment of three different fabrics can effectively reduce the drop in strength and increase the strength retention rate by about 5% compared with the commercial products. Analyzing the reason, under the influence of high temperature of resin finishing, the crosslinking speed is fast, and the stress of the fabric is concentrated, resulting in a decrease in strength. After hydroxylation, the activity of the modified 2D resin decreased, the crosslinking speed of the resin slowed down, and the stress concentration of the fabric decreased, so the strength performance of the fabric was improved[10].

Table 8. Influence of resin on fabric breaking strength.

| resin | Dosage (g/l) | NKC (g/l) | breaking strength (LB) |
|-------|--------------|-----------|------------------------|
|       | fabric 1     | fabric 2  | fabric 3              |
| ELF   | 80           | 24        | 36.17                  | 39.84                  | 51.1       |
| CR-E  | 80           | 24        | 39.43                  | 42.67                  | 55.5       |
| Blank Test | /           | /         | 49.43                  | 55.5                  | 70.43      |

Table 9. Influence of resin on fabric tearing strength.

| resin | dosage (g/l) | NKC (g/l) | tearing strength (N) |
|-------|--------------|-----------|----------------------|
|       | fabric 1     | fabric 2  | fabric 3              |
| ELF   | 80           | 24        | 5.29                  | 8.87                  | 3.73       |
| CR-E  | 80           | 24        | 5.89                  | 10.60                 | 4.21       |
| Blank Test | /           | /         | 9.82                  | 25.29                 | 6.26       |

3.3.2. Influence of whiteness and feel. According to the data in Table 10 and Table 11, the etherified modified 2D resin CR-E and the commercial products were treated with the two kinds of white fabrics respectively. It can be seen that the fabrics are colorless, the whiteness has little change, and the hand feel is slightly better than the commercial resin finishing agent products, which indicate that the properties of the etherified modified 2D resin CR-E prepared have reached the expectation.
Table 10. Influence of resin on whiteness of fabric.

| resin     | dosage (g/l) | NKC(g/l) | whiteness fabric 1 | whiteness fabric 2 |
|-----------|--------------|----------|--------------------|--------------------|
| ELF       | 80           | 24       | 136.15             | 135.92             |
| CR-E      | 80           | 24       | 136.29             | 137.34             |
| Blank Test| /            | /        | 144.44             | 143.89             |

Table 11. Influence of resin on fabric feel.

| resin | dosage (g/l) | NKC(g/l) | feel fabric 1 | feel fabric 2 | feel fabric 3 |
|-------|--------------|----------|---------------|---------------|---------------|
| ELF   | 80           | 24       | ++            | +             | +             |
| CR-E  | 80           | 24       | ++            | ++            | +             |

Note: The more +, the better it feels.

3.3.3. Influence on the ironing property of resin. According to the data analysis in Table 12, the comparison between the etherification modified 2D resin CR-E and the resin products on the market for the treatment of the three fabrics shows that the ironing fastness of the fabrics will be improved to a certain extent. The effective amount of 2D resin and the covalent cross-linking degree of cellulose fiber were reduced, and the cross-linking activity of etherified resin and fiber was decreased, and the wrinkle recovery Angle was decreased, but it was slightly higher than that of resin finishing agent products sold on the market, which reached the requirement of durable and ironing finishing.

Table 12. The influence of resin on the ironing property of fabrics.

| resin | dosage (g/l) | NKC(g/l) | Free ironing grade DP fabric 1 | Free ironing grade DP fabric 2 | Free ironing grade DP fabric 3 |
|-------|--------------|----------|-------------------------------|-------------------------------|-------------------------------|
| ELF   | 80           | 24       | 3.0                           | 3.0                           | 2.9                           |
| CR-E  | 80           | 24       | 3.0                           | 3.1                           | 3.0                           |

3.3.4. Influence on fabric formaldehyde. As can be seen from Table 13, through the application performance analysis of 2D resin etherified modification and commercially available ELF resin products, it can be seen that the newly prepared etherified 2D resin product has lower free formaldehyde content (the national standard GB18401-2001 specifies that the skin type is directly removed ≤75mg/kg). The reason is that after etherification, the 4-5 hydroxyl groups of 2D resin are etherified, which reduces the formaldehyde content released.

Table 13. Influence of resin on formaldehyde in fabric.

| resin | dosage (g/l) | NKC(g/l) | Formaldehyde mg/kg fabric 1 | Formaldehyde mg/kg fabric 2 | Formaldehyde mg/kg fabric 3 |
|-------|--------------|----------|----------------------------|----------------------------|----------------------------|
| ELF   | 80           | 24       | 36.56                       | 44.25                       | 40.25                       |
| CR-E  | 80           | 24       | 33.75                       | 44.25                       | 38.25                       |

4. Conclusion

Compared with the traditional method, 2D resin one-step synthesis process has simplified the process flow, shortened the reaction time and improved the reaction efficiency. The optimal reaction conditions of 2D resin synthesis were determined as follows: mass ratio N (glyoxal) : N
(formaldehyde) : N (urea) =1:1:1.8, pH 6.0-6.5, temperature 60℃, time 4h, the content of free formaldehyde of the synthesized 2D resin was less than 0.5%.

Through the modification of 2D resin, the content of free formaldehyde in textile fabrics was further reduced, and the ironing and wearability of textile fabrics were improved. Through experimental analysis, the optimal process of etherification modification was determined as follows: the amount of methanol (relative to the amount of 2D resin) was 35%, the temperature was 50℃, the time was 3h, the pH value was 1.5 ~ 2.0, and the amount of free formaldehyde in the etherified resin was less than 0.2%. At the same time, compared with the commercially available ELF resin, the properties of the etherified modified 2D resin, such as breaking strength, tearing strength and whiteness feel, are better and have a good market promotion value.

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