Preparation and Application of Waterborne Polyurethane with Starch as Soft Segment

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Abstract. The preparation of waterborne polyurethane was studied when starch acted as soft segment. The reaction conditions of preparation about the waterborne polyurethane were discussed. The infrared spectrum was used to characterize the copolymer emulsions. At the same time, the applications of the prepared starch-TDI copolymer emulsions were researched on paper coating and wet end addition in this paper. It was showed that the prepolymerization time was 2 hours and the blocking time was 25 minutes. The results of applications showed that the physical properties were improved obviously after coating or wet end addition. In addition, it was found that the coated papers had better enhancement effects than the wet end added papers.

Keywords: Starch-TDI Copolymer Emulsions, Preparation, Coating, Wet End Addition, Physical Properties

1 Introduction
In the previous researches[1-2], polyethylene glycol-400 (PEG-400) was used as the soft segment to react with toluene-2,4-diisocyanate (TDI) in order to form prepolymers, then sodium bisulfite was used as the blocking agent to block the remaining isocyanate(-NCO) groups by the blocking and unblocking mechanism of -NCO. It was found that the unblocked -NCO groups reacted with the hydroxyl groups on the fibers[3], and the hydrogen bonds were converted into the chemical bonds. As a result, the physical properties (especially the wet strength) of the paper were greatly improved and the printability of the paper was also improved.

The problem of short chains was solved by PEG when it was soft segment. And the results showed that the enhancement effect of the treated paper was good. However, there were many disadvantages, such as high cost and poor environmental protection etc. In this paper, starch was selected as the soft segment. On the one hand, starch had a lot of hydroxyl groups which could synthesized prepolymer with TDI. On the other hand, starch itself was a common papermaking assistant and it have contributed to the physical properties of papers. Starch was innovative selected to react with TDI in the paper, and then the residual isocyanate (-NCO) groups were blocked by sodium sulfite[4]. Starch-TDI copolymer emulsions were prepared and applied to paper coating and wet end addition. It was found that the enhancement effects were good and the physical properties of papers were obviously improved.
2 Experiment

2.1 Reagent
The used reagents in the experiment were as follows: TDI(Analytical pure), sodium bisulfite(Analytical pure), anhydrous sodium sulfate(Analytical pure), di-n-butylamine (Analytical pure), bromophenol blue indicator(Homemade), pregelatinized starch (Hebei Shuangyuan cellulose factory), 0.1mol/l hydrochloric acid standard solution (Homemade).

2.2 Preparation of Waterborne Polyurethane
A certain amount of pregelatinized starch and ethyl acetate (solvent) were proportional added into a 250ml three-port flask equipped with a thermometer, a stirrer and a reflux condensing tube. Then the flask was put into an oil bath at 70°C and the solution was stirred evenly. At the same time, a calculation amount of TDI was added and the content of -NCO groups in the system was measured by di-n-butylamine after a period of reaction\[5\]. When the content of -NCO groups reached a certain value, it was cooled down to 0~5°C by ice bath. Then the calculated amount of sodium bisulfite was added to block the reaction. At the same time, the amounts of -NCO groups were detected. The starch-polyurethane prepolymer was obtained after the blocking reaction was finished, and then the waterborne polyurethane (Also called starch-TDI copolymer emulsions) was prepared by dispersing it in water at high speed.

2.3 Coating
The prepared starch -TDI emulsion was evenly coated on the blank papers (handsheet), and then the papers were dried to form the coated papers on the oven.

2.4 Wet End Addition
A certain amount of the dried paper pulps was weighed and broken up in the dfibizer. The blocked starch-TDI emulsions were added to the dispersed pulp according to different amounts. At the same time, they were continuously stirred by the stirrer in order to make the polymers react with the fibers completely. After the papers were made, they were dried at 80~90°C on the oven.

2.5 Determination Method
According to the national standard, the papers were tested for breaking length, wet strength, tearing resistance, folding endurance, bursting strength, whiteness and sizing degree.

3 Results and Discussion

3.1 The Relationships between the Prepolymerization Time of Starch-TDI and the Content of NCO Groups
The relationships between the prepolymerization time of starch-TDI and the content of NCO groups were showed in Table 1. As shown in Table 1, at the beginning of prepolymerization, the content of NCO groups was decreased sharply, however, the content of NCO groups was decreased slowly after 2 hours. In order to meet the requirements of the experiment, 2 hours was selected as the reaction time in this experiment.

| Time/h | Mass of prepolymer/g | Volume of hydrochloric acid consumed/ml | The content of NCO/% |
|--------|----------------------|----------------------------------------|---------------------|
| 1      | 2.1                  | 2                                      | 12.29               |
| 2      | 2.1                  | 39.2                                   | 2.598               |
| 3      | 2.1                  | 44.1                                   | 1.292               |
| 4      | 2.1                  | 46.5                                   | 0.598               |
| 5      | 2.2                  | 47.6                                   | 0.269               |

Note: The consumption of hydrochloric acid for blank sample was 48.5ml.
3.2 Relationships between Reaction Time and the Closure Rates of Prepolymers
When the content of NCO groups reached the predetermined value, the prepolymers would be taken out. Appropriate amount of blocking agent, accelerator and solvent were added to react with them to form the prepolymers, and the prepolymers were blocked under the environment of below 5 °C [6]. The closure rates were measured under different blocking time.

The determination steps were as follows: the samples were weighed 5g into a 250ml conical flask, and the solvents were added to dissolve them, then they were titrated with I₂ solution to the end point. The end point was the end point of free bisulfite in the solution, the titration volumes were recorded V₁. Then the 10ml NaOH solutions were added, and H₂SO₄ solutions were also added for acidification after 2 minutes, and they were titrated to the end point with I₂ solution. The titration volumes were recorded V₂. The relationships between reaction time and closure rates of prepolymers were showed in Table 2. It could be seen from Table 2 that the closure rates were rapidly increased at 0~25 minutes, and there was minor changes after 25 minutes. As a result, 25 minutes was selected as the blocking time in this experiment. The calculation formula of closure rates was as follows:

\[
\text{Closure rate} = \frac{V_2}{(V_1 + V_2)} \times 100\%. \quad (1)
\]

Table 2. Relationships between reaction time and closure rates of prepolymers

| Time/h | V₁/ml | V₂/ml | Closure rates/% |
|--------|-------|-------|-----------------|
| 0      | 0     | 12.6  | 0               |
| 5      | 9.5   | 15.4  | 57              |
| 10     | 7.2   | 16.7  | 68              |
| 15     | 5.5   | 17.3  | 75              |
| 20     | 4.2   | 19.2  | 80.5            |
| 25     | 3.1   | 18.6  | 86.1            |
| 30     | 2.1   |       | 89.8            |

3.3 Characterization of the Starch-TDI Copolymer Emulsions
The physical properties of starch-TDI copolymer emulsions were showed that the color was milky white, the solid content was 40%, and the viscosity was 2.4 Pa·s. After vacuum drying, the infrared spectra of the starch-TDI copolymers was determined on NICOLET FTIR 170SX infrared spectrometer, and the IR spectra was showed in Figure 1.

As everyone knows, the amino stretching vibration of carbamate often occurs at 3450~3225 cm⁻¹. It appeared together with hydroxyl groups at 3385.51 cm⁻¹ in the spectra of Fig.1 [7]. The carbonyl peak of carbamate was found at 1648.52 cm⁻¹. The band of carbamate often appears at 1090~1050 cm⁻¹, and it was found at 1081.16 cm⁻¹ in the Fig.1. In addition, the strong peak appeared at 1610 cm⁻¹ indicated the existence of benzene ring. It was showed that TDI structures existed in the starch-TDI copolymer emulsions. The system may have the following reactions:

\[
\text{Starch-OH} + -\text{NCO} \rightarrow \text{Starch-OCONH} \quad (2)
\]

Fig.1 Infrared spectra of starch-TDI copolymers
3.4 Coating Effect of the Starch-TDI Copolymer Emulsions

According to the national standard, the physical properties of the papers such as wet strength, tearing resistance, bursting strength, folding endurance, whiteness and sizing degree were tested, and the test results were showed in Table 3. It was showed that the physical properties of the coated papers were stronger than the blank papers. The wet strength, tearing resistance, bursting strength, folding endurance were obviously improved but the whiteness was not changed much in Table 3. In addition, the breaking length was increased by 2.32 times, and the wet strength was increased by 5.69 times, at the same time, the wet/dry strength ratio reached 18.0%. The mainly reason was that the blocked isocyanate groups were unblocked after heating, and the unblocked isocyanate groups reacted with the hydroxyl groups on the fibers of the papers to form the carbamate bridge structures in the process of drying. As a result, the physical properties of the coated papers were obviously improved.

Table 3. Physical properties of blank papers (I) and coated papers (II)

|                | Wet strength / Km | Breaking length / km | Tearing resistance /mN | Bursting strength /KPa | Folding endurance /frequency | Whiteness /%ISO | Sizing degree /s |
|----------------|-------------------|----------------------|------------------------|------------------------|----------------------------|-----------------|-----------------|
| I              | 0.119             | 1.617                | 2.5                    | 75.0                   | 12                         | 76.4            | 0               |
| II             | 0.678             | 3.758                | 3.4                    | 120.9                  | 54                         | 75.9            | 110             |

Note: The coating amount was 10g/m² and the wet strength was the tensile strength which was measured after soaking the papers in the water for 24 hours.

3.5 The Effect of Starch-TDI Copolymer Emulsions as Wet End Additive

The test results of physical properties of blank papers and wet end added papers were showed in Table 4. As shown in Table 4, there was little changes about the whiteness and the folding endurance of the wet end added papers compared with the blank papers. However, wet strength, breaking length, bursting strength were increased obviously. At the same time, the physical properties of wet end added papers were worse than the coated papers. In other words, the coated papers had better enhancement effects than the wet end added papers. The mainly reason was that the most of the unblocked isocyanate groups reacted with water to form urea and carbon dioxide. In addition, they were also possible to cross-linking themself to generate polyurethane. As a result, there were few carbamate bridge structures formed between fibers. In this way, the physical properties of the wet end added papers mainly depended on the hydrogen bonds between the fibers. The carbamate chemical bonds between the fibers had little contribution to the improvement of the physical properties of the wet end added papers. In a word, the coated papers had better enhancement effects than the wet end added papers.

Table 4. Physical properties of blank papers (I) and wet end added papers (II)

|                | Wet strength / Km | Breaking length / km | Bursting strength /KPa | Folding endurance /frequency | Whiteness /%ISO |
|----------------|-------------------|----------------------|------------------------|----------------------------|-----------------|
| I              | 0.116             | 2.014                | 341                    | 375                       | 76.1            |
| II             | 1.012             | 2.352                | 356                    | 369                       | 74.5            |

4 Conclusion

(1) Starch was innovative selected as soft segment in this experiment. On the one hand, starch had a lot of hydroxyl groups which could synthesized prepolymer with TDI. On the other hand, starch itself was a common papermaking assistant and it have contributed to the physical properties of papers.

(2) During the preparation of waterborne polyurethane, the temperature should be controlled at 70℃, and the reaction time should be 2 hours. During the blocking process, the temperature should be controlled below 5℃ in order to avoid the reaction between NCO groups and water. The blocking time was 25min.
(3) The coated papers had better enhancement effects than the wet end added papers. The main reason was that the most of the unblocked isocyanate groups reacted with water to form urea and carbon dioxide when the forming of the wet end added papers, and the carbamate bridge structures between fibers were very few, so that the physical properties of papers mainly depended on the hydrogen bonds between fibers and the carbamate chemical bonds between fibers made little contribution to the improvement of physical properties of papers.

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