Study on the tannery waste in the preparation of cement foaming agent

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Abstract: A global demand for efficient re-utilization of tannery waste, which is based on the principles of re-use and recycling, results to a circular economy, where one industry's waste becomes another's raw material and it can be used in a sustainable way. In this study, the collagen in the waste shavings is extracted by hydrolysis with sodium hydroxide. Then, using benzene as a solvent, natural rosin as a raw material, phosphorus trichloride is used as a chlorinating agent to react with natural rosin to obtain rosinyl chloride, and rosinyl chloride is reacted with collagen to prepare a novel anionic surfactant. Lauryl alcohol continued to improve its stability, and the results showed that the overall performance was best when the amounts of SDBS and dodecyl alcohol were 0.25% and 0.6%, respectively. The performance of the obtained foaming agent was tested. The experimental data show that the foaming agent is obtained in this experiment, the foaming height reaches 147mm, and the half-life reaches 580s.

1. Introduction

Collagen is the main component of leather. If the waste shavings are not recycled, it will have a great adverse effect on the ecology and waste a lot of protein resources. Among the building insulation materials, organic insulation materials have many advantages, but organic insulation materials have hidden dangers, which is one of the causes of fires in buildings (Chen et al., 2009; U.S. EPA, 1986). Foamed concrete has also appeared in people's field of vision. The excellent performance of foam concrete itself has been widely welcomed in the building materials market. Foamed concrete is a building material, which is an insulating material made by mixing, pouring, curing, etc.

The tannery solid waste contains a large amount of collagen, and the side chain amino group of the basic amino acid such as lysine or arginine in the collagen has high activity and can undergo a nucleophilic reactions (Abreu and Toffoli, 2009; Swarnalatha et al., 2006). The common chemical reactions of amino groups are amination, amidation and phosphorylation. Amidated surfactants have good foaming properties, high safety and good detergency, so they are used in shampoos, cleaning agents, soaps, etc (Celary and Sobik-Szołtysek, 2014; Silva et al., 2010).

Rosin is a complex natural mixture whose physicochemical properties depend on the various chemical reactions that resin acids can form. The resin acid molecule has two chemical reaction centers: a double bond and a carboxyl group. Rosin is actually a kind of oil that flows out of plants. It will form rosin when processed simply. In the construction of the project, rosin soap prepared by adding rosin as main material, rosin soap prepared by heating reaction and rosin and phenol, sulfuric acid and other materials are widely used as raw materials. Air entraining agent, which acts to improve the fluidity, frost resistance, pumpability, workability, etc. of concrete by forming extremely fine, closed bubbles. For example, if concrete is to be pumped for high-rise building, Air entraining agent needs to be added, otherwise the pump can't be transported to the top of the high-rise. Only other construction schemes can be taken. In this paper, rosin is combined with collagen to try to develop a characteristic of a tiny fine foam with both rosin and a foam-rich foaming agent.

This topic combines chrome shavings with rosin to develop a new type of concrete foaming agent. Compared with the traditional foaming agent, it not only solves the pollution problem of the tanning industry, but also has obvious economic benefits.

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2. Materials and methods

2.1 Experimental instruments and reagents

The Roche foam meter used in this study is an instrument produced by China's Longkou City Advanced Instrument Company. Sodium dodecyl benzene sulfonate (AR) lauryl alcohol (AR) and phosphorus trichloride (AR) are the Tianjin Branch of China, provided by the Miou Chemical Reagent Development Center, leather shavings and rosin are industrial products supplied by the Yantai Wendeng Tannery in China.

2.2 Hydrolysis of leather shavings

The leather shavings are dried in an oven to constant weight, accurately weighed to 0.01g, and then placed in a three-necked flask. According to the designed experimental scheme, water, alkali, and a constant temperature water bath are set to a fixed temperature, and the stirring paddle is installed, thermometer, cooling water. After the temperature rise is completed, the speed switch is turned on, and the set speed is 25r/min. After the set time is reached, it is stopped, taken out into the beaker and lowered to room temperature. The centrifuge is used to extract the hydrolyzate first, and then through the filter. A pure protein hydrolyzate was obtained after secondary purification.

The molecular weight of the hydrolyzate after demineralization was measured by GPC (gel chromatography) method, and polyethylene glycol was used as a standard, and a gel permeation chromatograph was used, and a sodium nitrate buffer was used as a mobile phase.

2.3 Preparation of rosin acyl surfactant

In this experiment, rosin resin is used as raw material, phosphorus trichloride is used as chlorinating agent, and benzene is used as solvent to prepare rosin acid chloride. The procedure is to first grind the rosin and then dissolve it with benzene. In a ventilated kitchen, stir it with a magnetic stirrer. The next drop was added with phosphorus trichloride, and the reaction was continued for 3 hours after the completion of the dropwise addition, after which the oil phase was separated by a separatory funnel and the rosin chloride was extracted by extraction. The polypeptide hydrolyzate was added to a five-necked flask, and rosin chloride and sodium hydroxide solution were slowly added under stirring with a magnetic stirrer to maintain a constant pH. After the reaction was completed, the pH was adjusted to 2 using concentrated hydrochloric acid, and a precipitate appeared in the five-necked flask. Filtration gave a yellow precipitate which was washed with petroleum ether to give a rosinyl peptide surfactant.

2.4 Performance complex and Performance test

Based on the rosinopeptide surfactant, the foaming component and the stabilizing component were further added to further improve the foam properties. The single factor experiment was used to explore the effect of each component on the foam properties. adding SDBS and dodecyl alcohol to improve its performance. In this experiment, the foaming agent was tested for foaming height and half-life using a Roche foamer.

3. Results and discussion

3.1 Molecular weight analysis of hydrolysate

The number average molecular weight obtained after desalting and purifying the protein hydrolyzate obtained above by a dialysis bag having a molecular weight cut off of 1000 is shown in Table 1.

As can be seen from Table 1, the highest molecular weight obtained by hydrolysis is 14365 Da, and the lowest is 9194Da. It can be seen that as the hydrolysis rate increases, the molecular weight of the hydrolyzed protein product gradually decreases. The hydrolysis temperature, the alkali amount, and the solid-liquid ratio all affect the number average molecular weight. The important factors are the amount of alkali > hydrolysis temperature>solid-liquidratio> hydrolysis time, and hydrolysis time is a relatively minor factor. The protein foam with the molecular weight between

8000-30000 has the best performance. At the same time, the larger the molecular weight, the stronger the foam stability. The above factors and the cost are the most suiTable for the hydrolysis of the foaming agent: hydrolysis The temperature is 70 °C, the amount of alkali is 11%, the ratio of solid to liquid is 1:8, and the hydrolysis time is 5 hours. At this time, the molecular weight is 14356Da.

Table 1 Hydrolyzate number average molecular weight

No.	Hydrolysis	NaOH	Solid-liquid	Hydrolysis	Molecular
	temperature(°C)	dosage(%)	ratio	time(h)	weight(Da)
1	70	11	1:8	5	14365
2	80	11	1:10	6	13992
3	90	11	1:12	7	9430
4	80	13	1:8	7	12041
5	90	13	1:10	5	10279
6	70	13	1:12	6	11739
7	90	15	1:8	6	9194
8	70	15	1:10	7	10857
9	80	15	1:12	5	9919
K1	11820.333	12595.667	11866.667	11521.000	
K2	11984.000	10853.000	11709.333	11141.667	
К3	9634.333	9990.000	9862.667	10776.000	
Max-Min	2349.667	2605.667	2004.000	745.000	

3.2 Effect of different factors on synthetic protein-based surfactants

The optimum synthesis conditions and the influence of various factors on the reaction were analyzed by orthogonal experiments, and the results are shown in Table 2.

Table 2 Synthetic protein-based surfactant orthogonal experiment results

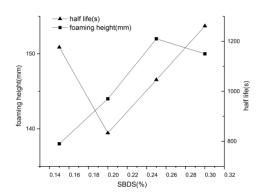
No.	temperature(°C)	рН	Hydrolyzate(%)	Volume ratio	Conversion rate(%)
1	40	8	15	1	83.36
2	50	8	20	0.5	78.39
3	60	8	25	0.75	72.53
4	40	9	25	0.5	71.23
5	50	9	15	0.75	74.94
6	60	9	20	1	73.56
7	40	10	20	0.75	70.75
8	50	10	25	1	74.81
9	60	10	15	0.5	86.93
K1	75.113	78.093	81.743	77.243	
K2	76.047	73.243	74.233	78.850	
K3	77.673	77.497	72.857	72.740	
Max-Min	2.560	4.850	8.886	6.110	

It can be seen from the above Table that the most important factor affecting the conversion rate of the amide reaction is the content of the hydrolyzate, the content of the hydrolyzate is high, and the amino group content for the reaction is high, so the conversion rate of the amide reaction proceeds in the positive direction, and the volume ratio is also An important factor affecting the progress of the reaction is mainly due to the side reaction of hydrolysis of rosin chloride in the reaction. If the amount of water is too large, the reaction tends to proceed in the direction of hydrolysis of rosinyl chloride.

3.3 Performance test result

In this experiment, the foaming height and half-life of the obtained compound solution were

tested by a Roche foamer, and the data obtained at a concentration of 5g/L is shown in the figure below.



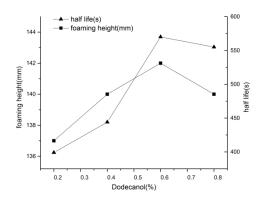


Fig.1 Effectof SDBD contenton the performance of foaming agent

Fig.2 Effect of Decylene Contenton Foaming Performance

It can be seen from Fig. 1 that the foaming ability of the compounding foaming agent at a concentration of 5g/L has reached a peak at a SDBS content of 0.25% because the SDBS after this concentration is at this concentration. The micelles formed in the solution, so that no more foam can be produced, and the half-life does not have a certain regularity, so the total amount of SDBS used above is determined to be 0.25%.

The incorporation of lauryl alcohol can form a two-layer film together with the surfactant at the gas-liquid interface, mainly because lauryl alcohol is an alcohol that is less dense than water and insoluble in water, and can be arranged together with a surfactant. At the interface, but excessive doping can affect the electric double layer effect of the surfactant and make the foam easily broken.

4. Conclusions

The most suitable hydrolysis conditions for the blowing agent are: hydrolysis temperature 70°C, alkali dosage 11%, solid-liquid ratio 1:8, hydrolysis time 5 hours, at which time the molecular weight is 14356Da. The highest conversion rate in the rosinyl chloride synthesis experiment It was 86.93%, the condition was temperature 60°C, the hydrolyzate accounted for 15%, the pH was 10, and the volume ratio was 0.5. In the foaming performance compounding, the optimal addition amount of SDBS is 0.25%. In the stability energy compounding, the addition amount of dodecyl alcohol is the best at 0.6%, so the optimal conditions for the compounding are: 0.25% of SDBS and 0.6% of dodecyl alcohol.

With the increasing pollution of the natural environment around the world and the intensification of the world energy crisis, the tanning industry is facing the test of sustainable development, which is the most effective way to reduce the pollution of the tanning industry and how to deal with the waste of the tanning industry. It is two aspects that the tanning industry pays particular attention to. In this study, not only the hazardous waste such as waste leather shavings was utilized, but also a new type of high-efficiency cement foaming agent was prepared, which not only meets the engineering production needs, but also has low cost and can achieve very good economic benefits.

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