Study on the Preparation of Oil Gelling Agent from Chrome Shavings

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Abstract: The collagen was extracted from chrome shavings with alkali. Through the carboxyl methylation, acylation and deposition with metal ions, the oil gelling agent was obtained. Moreover, the effect of carboxymethylation degree, acyl chloride degree and the categories of metal ions on preparation reaction were discussed. The better preparation condition was obtained. In carboxymethyl reaction the weight ratio of sodium chloroacetate and collagen was 1:2; in acylation the weight ratio of oleoyl chloride and collagen was 3:1; in deposition with metal ions the effect of aluminum was best. The structural characterization of prepared oil gelling agent was carried out by IR spectrum and the results showed its oil gelling effect was good.

Key words: oil gelling agent, chrome shavings, collagen, modification

1 Introduction

China is a big tanning country. A great deal of chrome shavings will be produced in every year. The main component of these shavings is collagen and it is a kind of valuable natural resource. The offal can not be completely used, so it causes severe pollution to environment. [1] In order to discovering suitable using approaches for these leather shavings, many researchers have been doing much work. Through the deep research to collagen, a new phase for the using of chrome shavings is pioneered. Extracting collagen from chrome shavings, modifying the collagen and making use of them in other areas have become a popular topic inside and outside nation. [2-5]

A lot of oil is leaked out on the sea all over the world; as a result, the leaked oil has caused severe pollution to environment. To preventing oil pollution, the international and every country along the sea have made a series of rules and conventions, and they also pay more attention to the treatment, recycling and removing technologies to leaked oil. Firstly, the spilled oil was restricted to diffuse (using fence, oil gathering agent), then we use oil gelling agents or oil absorbing materials to coagulate. Finally, we can use machinery to recycle the residual oil. For the extremely few remaining oil, whose layer thickness is less than 0.05cm, emulsification and biological methods can be used to deal with.[6]

When the oil layer thickness is between 0.05cm and 0.3cm, generally the oil gelling agent is used to deal with it. The principle is for its hydrophobic and oleophilic property. It can form net structure with oil and then plenty of oil and little water can be packed in the net to shape into an oil micelle, which can be removed by salvage. At present, there are many categories of oil gelling agents, such as aminophenol, alcohol ramification, fatty acid ramification and

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protein.[7-8]

Considering the reuse of chrome shavings and eliminating pollution of leaked oil to the sea, and combining the action principle of proteinic oil gelling agent, in the experiment we extracted collagen from chrome shavings and modified it to prepare collagen oil gelling agent. Moreover, the oil gelling test was also carried out.

2 Experimental sections

2.1 Materials and apparatus

Pig chrome shavings were produced by Leather-making Co., Ltd (Shandong province, Yantai city). Magnesium oxide (AR) was supplied by Dengfeng chemical reagent factory (Tianjin province). Lauryl sodium sulfate (AR) was provided by Xi'an Chemical Reagent Company. Phosphorus trichloride is supplied by Hengda Chemical reagent CO., Ltd (Shanghai province); Sodium chloroacetate (CR) was provided by Bodi Chemical reagent CO., Ltd (Tianjin province); Oleic acid, aluminum sulfate、ferric chloride and calcium oxide (AR) all are provided by Tianjin Chemical Reagent Company.

DHG-101A-1C constant temperature blast desiccator was offered by Shanghai Shendang Zhongxin electrical equipment Factory; VECTOR-22 IR Spectrum apparatus provided by Germany Bruke Company; ZXZ-1 revolving vacuum pump was supplied by Zhejiang Precision Vacuum Apparatus Factory; OLYPUS digital camera offered by Japanese Company.

2.2 Extraction of collagen

Because only long-chain protein can be used to prepare proteinic oil gelling agent, the magnesium oxide was chosen to extract collagen from chrome shavings. The extracting process was as follows:

Pig chrome shavings were weighed up 50g, adding to 250g water to make it moist, and then add 0.1% lauryl sodium sulfate and 6% magnesium oxide (calculated on the basis of pig chrome shavings weight). The reaction was kept 6h under 70℃. By filtrating the collagen was obtained.

2.3 Preparation of oleoyl chloride

The fatty acid acyl chloride was synthesized by phosphorus trichloride and fatty acid. Its reaction equation was as follows.[9]

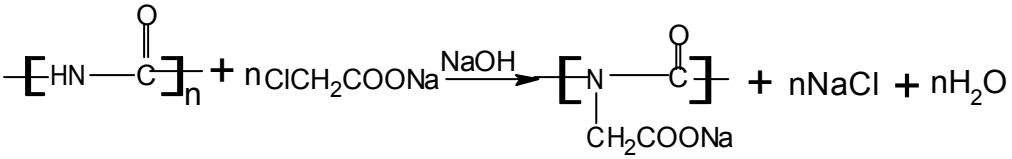
$$3C_{17}H_{33}COOH + PCl_3 \longrightarrow 3C_{17}H_{33}COCl + H_3PO_3$$

Oleic acid was weighted up and added into three-mouth flask, slowly dripping phosphorus trichloride to it. The temperature was kept at 25~33 ℃. After adding it raising temperature to 55 ℃ and reacting 4h. Standing 4h and then separating the lower orthophosphorous acid, the oleoyl chloride was obtained. 50% oleoyl chloride acetone solution was prepared by mixing oleoyl chloride and acetone whose quality ratio was 1:1 and then keep it in brown bottle.

2.4 Preparation of oil gelling agent[10-11]

2.4.1 Carboxymethylation reaction of collagen

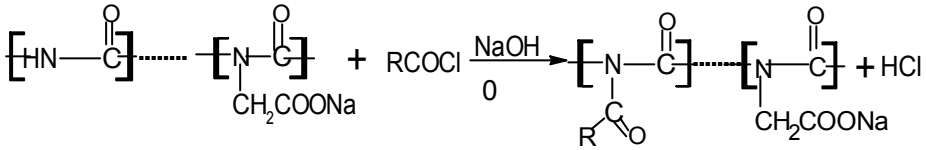
The carboxymethyled collagen was synthesized by the reaction of collagen and chloroactic acid under alkali condition. The reaction was shown as follows:



The extracted collagen was weighted up 11g (its quantity of peptide bond is 0.25mol) and water is 50mL, adding into three mouth flask. The reaction temperature is 40℃. When collagen was completely dissolved, adding certain quantity of sodium chloroacetate and then react 2h. In the reaction process sodium hydroxide whose mass fraction is 40%～45% was used to adjust pH to 7.0-8.0. After finishing the reaction the temperature was raised to 70℃ and continue to react for 2h. In the process pH was kept 7.0～8.0.

2.4.2 Acylation reaction of carboxymethyled collagen

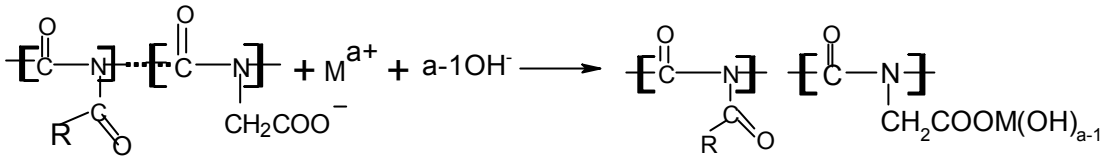
Through the reaction of carboxymethyled collagen and prepared oleoyl chloride under lower temperature, the acylated carboxymethyled collagen was obtained. The reaction formula was as follows:



The synthesized carboxymethyled collagen was cooled to 0～5℃, adding 15g acetone and alternatively dropping 30g mixture of oleoyl chloride and acetone whose mass quantity is 50% and 45% sodium hydroxide. During the reaction pH was kept 9～10 for 3h.

2.4.3 Deposition with multivalent metal ions

Under certain pH, multivalent metal ions were used to deposit the acylated carboxymethyled collagen. The reaction process was shown as follows:



Some water(calculated basing on viscosity of reaction liquor) was added into above reaction system to diluting it, and then adjusting pH to 6.0～7.0 with 1：1 hydrochloric acid. After fully stirring 20% metal ions liquor was dropped. Slowly dropping 45% sodium hydroxide to increase pH until granular solid or floccules was appeared.

2.4.4 Washing and drying

Filtring above liquor using gauze and washing the obtained granular solid in beaker, then carrying out centrifugal dewatering for 20～24h. The vacuum degree was 68～82Kpa and temperature was 20～30℃. After grinding the dried granule, the light yellow dusty oil gelling agent was obtained.

2.5 Applying experiment of coagulating oil

The 60g water was added into a glass-surface vessel whose area was 86cm2 and highness was 2cm. Dripping 3g crude oil into glass-surface vessel and its thickness was about 0.05cm. The prepared oil gelling agent was added into the system and kept for 5min. Its dosage was 70% (basing on the quantity of crude oil). Observing the phenomena and calculating the quantity of absorbed crude oil.

2.6 Characterization

2.6.1 Characterization of coagulated oil quantity

The way to evaluating property of oil gelling agent is to calculating the quantity of coagulated oil with one gram oil gelling agent, but there wasn't accurate apparatus or recognized standard method to test it. In the experiment we adopted following method to represent.

Weighing the quality of dried beaker and showing as M_0. Through filtration with four-layer gauze, the oil gelling agent, crude oil and water can be separated. The quantity of filtrate and beaker was showed as M_1. So the quantity of oil micelle containing water equals water quantity (60g) plus crude oil quantity plus oil gelling agent weight subtract the difference of M_1 and M_0.

2.6.2 IR spectral analysis

The extracted collagen and prepared oil gelling agent were respectively ground into powder, and then testing them by pressing potassium bromide troche.

2.6.3 Observation of coagulating oil test

The state changes of oil before and after coagulated by oil gelling agent were screened by digital camera.

3 Results and Discussion

3.1 Single-factor experiment of oil gelling agent preparation

3.1.1 The effect of carboxymethylation

The aim of carboxymethylation was to introduce hydrophobic groups into collagen molecule and reduce its solubility. So the dosage of sodium chloroactate determined the density, solubility and lipophilicity of oil gelling agent. Controlling other factors were the same and changing the mol ratio of collagen peptide bond and sodium chloroactate which respectively was 5:1、4:1、3:1、2:1、5:4 and 1:1. Under the condition the test was carried out.

The results showed that when mol ratio of peptide bond and sodium chloroactate was more than 3:1, the prepared oil gelling agent is soluble. So it can't be used as oil gelling agent. When mol ratio of peptide bond and sodium chloroactate was less than 2:1, the hydrophobicity of prepared oil gelling agent was excellent and it has the effect of oil coagulation. With the increase of sodium chloroactate dosage, more hydrogen atoms in peptide bond were substituted. In following acylation hydrogen atoms which can be substituted reduced. The decrease of lipophilic groups caused reducing of lipophilic property. When mol ratio of peptide bond and sodium chloroactate was 1:1, nearly all hydrogen atoms were substituted. So collagen can't react with oleoyl chloride. As a result, the effect of coagulating oil became worse. According to the analysis we can see that when the mol ratio of peptide bond and sodium chloroactate was 2:1 in carboxymethylation, namely weight ratio of sodium chloroactate and pure collagen was 1:2, the effect of coagulating oil was the best.

3.1.2 The effect of acylation

The ester groups made carboxymethylated collagen has lipophilicity and form water-in-oil emulsion. Moreover, there were hydrophilic groups (such as amido group and hydroxyl) in collagen, the emulsion form oil gelatin. Because collagen has better solubility and has no lipophilic groups, pure collagen can't make water and oil system form gelatin. Increasing lipophilic groups of oil gelling agent can coagulate spilled oil on sea surface which is incapable of forming water-in-oil emulsion. Under the same condition the carboxymethylation

was carried out during which the dosage of collagen was 11g, and then modified with different quantity of oleoyl chloride. In deposition process the Al^{3+} as used without exception.

Tab.1 The effect of acylated reaction on coagulating oil

50% solution of oleoyl chloride and acetone(g)	phenomena of coagulating oil	Weight of oil micelle containing water(g)
0	Water was turbid, oil was viscous and not conglobation.	—
10	Granule float on surface, most oil dispersed.	7.125
20	Oil coagulated and become viscous, conglomeration was not obvious.	8.062
30	Black oil micelle conglomeration	9.084
40	Black oil micelle conglomeration	8.086

As shown in Tab.1, with the increase of oleoyl chloride dosage, the effect of coagulating oil became better and then worse, which because the reaction of oleoyl chloride and collagen took on saturation. When dosage exceeded the saturated value, the binding of oleoyl chloride and collagen was metastable and more oleoyl chloride remained in reaction system. Although oleoyl chloride increased, the quantity of lipophilic groups in collagen did not change. Basing on the test the following conclusions could be obtained. Keeping other reaction conditions were the same, when mass ratio of oleoyl chloride and collagen was 3:1, the effect of coagulating oil was the best.

3.1.3 The effect of ionic species

Under the same conditions, 11g collagen was modified by carboxymethlation and acylation in which the dosage of oleoyl chloride was 30g. Then deposited respectively with Al^{3+}、Fe^{3+} 、Ca^{2+} and Mg^{2+}. The coagulating oil test was done and prepared oil gelling agent were all 70% (basing on the weight of crude oil). The results were shown in Table 2.

Table 2 The comparison of oil gelling agents prepared by different ions

ionic species	phenomena of coagulating oil	Weight of oil micelle containing water(g)
Al^{3+}	Oil gelatin, water clear	9.146
Fe^{3+}	Oil gelatin, water clear	9.052
Ca^{2+}	Oil gelatin, water turbid	6.534
Mg^{2+}	Oil gelatin, water turbid	6.025

As shown in Table 2, Al^{3+} and Fe^{3+} took on excellent property of coagulating oil, but coagulating oil performance of Ca^{2+} and Mg^{2+} was worse. Owing to oil gelling agent prepared by trivalent ions had more active groups, could form more hydrogen bond and formative ions core was bigger and their structure was more stable, as a result, the oil micelle was more stable. Furthermore, the solubility of formative salts by carboxymethyl and trivalent ions was worse than that by carboxymethyl and divalent ions. So the prepared oil gelling agent by trivalent ions was difficult to be dispersed in water and the oil gelatin floated on surface, which proved its effect of coagulating oil was good. Because Fe^{3+} was rufous, during application process it

could influence water color, according to which $Al_2(SO_4)_3$ solution was chosen to be as precipitator. Considering the water consumption during modification and the clarity and turbidity of water after deposition, the dosage of 20% $Al_2(SO_4)_3$ was fixed in 70ml.

3.2 IR spectrum analysis

Compared with the IR spectrums of collagen and oil gelling agent, the characteristic peak of C=O in carboxylate carboxyl which appeared in 1650cm^{-1} and 1549cm^{-1} obviously becomes weak, which because carboxyl was closed by complexation with Al^{3+}. There was a peak in 3435cm^{-1} which is N-H in residual amide groups. The obvious peak of C-N in fatty tertiary amine appeared in 1124cm^{-1}, which showed that hydrogen atoms of amide groups in collagen are substituted.

3.3 Contrast figure of oil before and after coagulation

Adding 60g water in surface plate and dripping 3g crude oil, putting some oil gelling agent into it. Through screening we could obtain the figures in different steps. The figures before and after coagulating oil were as follows:

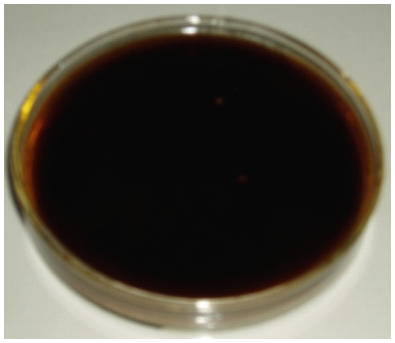


Fig.1 Before adding oil gelling agent

Fig.2 After oil gelling agent

Fig.3 The lateral observation of after oil gelling agent

As described in Fig.1, 2 and 3, the crude oil was dispersed on water surface. After adding oil gelling agent, the crude oil obviously agglomerated together and floated on water surface. This showed the effect of prepared oil agent was excellent.

4 Conclusions

In the experiment MgO was chosen to extract collagen from chrome shavings and its reaction condition was the dosage of MgO was 6%, lauryl sodium sulfate was 0.1%(calculated on the basis of pig chrome shavings weight), temperature was 70℃, the ratio of water and chrome shavings was 5.0 and reaction time was 6h. Under the condition the collagen with bigger relative molecular weight was prepared and it was suitable to be used for synthesis of oil gelling agent.

Through single factor test, the effect of carboxymethylated degree, acylated degree and the categories of metal ions on preparation reaction was discussed and the better synthesis conditions were obtained. In carboxymethylation, weight ratio of sodium chloroactate and pure collagen was 1:2, in acylated reaction, the mass ratio of oleoyl chloride and collagen was 3：1, in deposition with metal ions, $Al_2(SO_4)_3$ was chosen to be as precipitator and the dosage

of 20% $Al_2(SO_4)_3$ was 70ml.

The prepared oil gelling agent was used in simulation test of coagulating oil. The results showed that after adding oil gelling agent, the crude oil obviously agglomerated together and floated on water surface. This showed that the effect of prepared oil agent was excellent. The prepared oil gelling agent was insoluble and used raw material was collagen which was friendly environment, so the oil gelling agent was green for coastal water.

Acknowledgements

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