Synthesis of a New Crosslinker Microcapsule for Leather Finishing

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Abstract: A new crosslinker microcapsule for leather finishing was synthesized by interfacial polymerization. In this synthesis, hydrophobic carbodiimide crosslinker was chosen as core material and the reaction product of Hexamethylene diisocyanate (HDI) and polyamine was chosen as wall material. A preferred synthesis process was given as follow: phase weight ratio was 8:1, core and wall material weight ratio was 40:1, the reaction product of HDI and diethylenetriamine was chosen as wall material. The microcapsule size was 1～3μm, the microcapsule air tightness was 1.08%. The application of microcapsule polycarbodiimide (pCDI) showed the tensile strength was increased and the elongation at break was decreased, the microcapsule pCDI has better storage stability and the pot life of mixture of PU and microcapsule pCDI was prolonged.

Keywords: microcapsule; crosslinker; synthesis; storage stability; pot life

1 Introduction

Microcapsule technology is a protective technology. Microcapsule technology can protect the core materials because it can divided the core materials and the surrounding which can not only avoid the effect on light, oxygen, temperature and pH value but also can avoid the reaction between different substance. Making the core materials have the target and controlling release characters is a big performance for the microcapsule technology, which can release the core material at a proper time and place with a definite speed. In the application of finishing for leather, polycarbodiimide (pCDI) always was used as crosslinker. But along with the deposit time, pCDI will become viscous product even gel reacting with the reactive hydrogen. The normal preserving way is that pCDI crosslinker was kept in the nitrogen atmosphere in the obturator. But waterborne pCDI will still react with water until to gel slowly.

In this paper, microcapsule technology was used to resolve this problem. This microcapsule emulsion can afford better deposit condition for the crosslinker that insulating core material from the surroundings and prolonging the pot life. The microcapsule would be broken by the ironing and the drying machine when the microcapsule crosslinker was applied in the finishing process.

2 Experimental

2.1 Materials

Hexamethylene diisocyanate (HDI) was supplied by RHONE-POULENC（FRANCE）, 3-methyl-1-phenyl-2-phospholene-1-oxide (MPPO) was supplied by Bai Ling Wei Chemistry Technology Ltd. , Dimethylbenzene was supplied by Beijing Reagent Company. Polyvinyl alcohol (PVA) 1788 was supplied by Le Tai Chemistry Technology Ltd.

2.2 Preparation of crosslinker microcapsule

A 250ml round-bottomed, dried and four-necked separable flask with a mechanical stirrer, thermometer with a temperature controller was charged with 100g HDI and 0.5g catalyzer MPPO in dimethylbenzene (16%wt) and 100g amyl acetate. The mixture was heated to 120℃ for about 3h to

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obtain isocyanate terminated pCDI prepolymer. The change of -NCO value during the reaction was determined by a standard di-n-butylamine back-titration method. When the desirable average functionality was obtained, the prepolymer was cooled to 30℃. Then 66.3g di-n-butylamine was added in the reactant dropwise. While stirring, the mixture was heated to 30℃ for 1h～2h until no -NCO groups were detected, Then the system was cooled to normal temperature and the pCDI crosslinker was got.

Taking 100g the pCDI crosslinker and adding 1.34g HDI as oil phase. Then blend 4% sodium dodecyl benzene sulfonate and 0.3% PVA1788 as emulsifying solution. The above oil phase then poured, with vigorous agitation (shear velocity was 7000 r.p.m), into 800g emulsifying solution and an oil in water type emulsion was formed. When the size of the oil droplets was 1～3μm, transfer the mixture to three neck round-bottom. 1.17g diethylenetriamine as a polyamine was added to the emulsion, after stirring (velocity was about 400 r.p.m) the mixture for 10 minutes at room temperature, the temperature of the system was gradually raised to 60℃ and maintained at this temperature for a period of 2h. The microcapsule was got.

2.3 Characterization

2.3.1 Microscope picture

The microscope (CMM-55E, Shanghai Changfang Optical Instrument Co. Ltd.) was used to test the style and size of the microcapsule.

2.3.2 The size of microcapsule

The size of microcapsule was calculated from the microscope pictures by the scale.

3 Results and discussion

3.1 The effect of different phase weight ratio on the character of microcapsule

The protective collide PVA1788 (0.3%) and the sodium dodecyl benzene sulfonate (4%) were used as emulsifier solution. The effect of different phase weight ratio on the character of microcapsule was discussed.

From tab.1 we can see when the phase weight ratio was 8:1, the microcapsule with even distribution and small microcapsule size. When the phase weight ratio was very small, it is difficult to disperse and the microcapsule would be combined. So the microcapsule size is bigger and the quantity of the aggregation of the microcapsules would be larger. When the phase weight ration was very big, the shape of the microcapsule was irregular. The reason is that more emulsifier would accelerate the reaction speed of the isocynate and the amine and then the faster of the speed of the reaction the more irregular shape microcapsule. So the phase weight ratio of 8:1 was chosen.

Tab.1 The effect of different phase weight ratio on the character of microcapsule

Phase weight ratio	Appearance	Stability	The microcapsule distribution	Size of microcapsule (μm)
6:1	White emulsion	Broken after placed	Aggregation	1～8
7:1	White emulsion	Broken after 10 days	Aggregation	1～6
8:1	White emulsion	Stable	Even	1～3
10:1	White emulsion	Stable	Even，but the shape of microcapsule was irregular	1～3

Note: core and wall ratio=40:1; shearing and cutting time=10min

3.2 The effect of different core and wall ratio on the character of microcapsule

It is very important for the effect on the character of microcapsule to the core and wall ratio. The emulsifier solution was the same as 3.1. The effect of different core and wall ratio on the character of microcapsule was discussed.

Tab.2 The effect of different core and wall ratio on the character of microcapsule

Core and wall ratio	Appearance	Placed stabability	Size of microcapsule（μm）
20:1	White emulsion	Broken after 10 days	2～12
30:1	White emulsion	A little broken emulsion	2～10
40:1	White emulsion	Stable	1～3
50:1	White emulsion	Stable	3～8

Note: phase ratio=8:1; shearing and cutting time=10min

From tab.2 we can see when the core and wall ratio equaled 20:1 the microcapsule size was big, the distribution was uneven and the product is easy to break. It is because when the core and wall ratio was small, the wall material was increased relatively. With the thickening of the wall it is difficult to the free isocynate to transfer to the outside which inducing the polyurea deposition in the wall was more uneven. When the core and wall ration equaled 50:1, the microcapsule size was big and the distribution was uneven. It is because when the core and wall ratio was big, the core material was increased relatively. It is difficult to shear and induce the microcapsule size was bigger and the distribution was uneven. So the core and wall ratio of 40:1 was chosen.

3.3 The effect of different wall material on the character of microcapsule

The two different reaction products of HDI, ethylenediamine and HDI, diethylenetriamine were chosen as the wall material. The emulsifier solution was the same as 3.1. The effect of different wall material on the character of microcapsule was discussed.

From tab.3 we can see choosing the reaction product of HDI and ethylenediamine as wall material, the emulsion was broken after one month and the air tightness is poor. It is because the reaction product of HDI and ethylenediamine was linear structure. The enclosing character for the core was poor. With the lay time extending, the core material was exuded gradually which make the emulsion broke. If choosing the reaction product of HDI and diethylenetriamine as wall material, the product was net structure. The enclosing character for the core material was better and the hydrophobic core material was not easy to exude which make the emulsion is stable. So choose the reaction product of HDI and diethylenetriamine as wall material.

Tab.3 The effect of different wall material on the character of microcapsule

Wall material	Appearance	Stability	Size of microcapsule（μm）	Air tightness （%）
HDI and ethylenediamine	White emulsion	Broken after one month	2～5	5.64
HDI and diethylenetriamine	White emulsion	Stable	1～3	1.08

Note: core and wall ratio=40:1; phase ration=8:1; shearing and cutting time=10min

4 The microscope picture of crosslinker microcapsule

Fig.1 shows the microscope picture of crosslinker microcapsule. From this fig.1 we can see the distribution of the microcapsule was even and the microcapsule size was about 1～3μm.

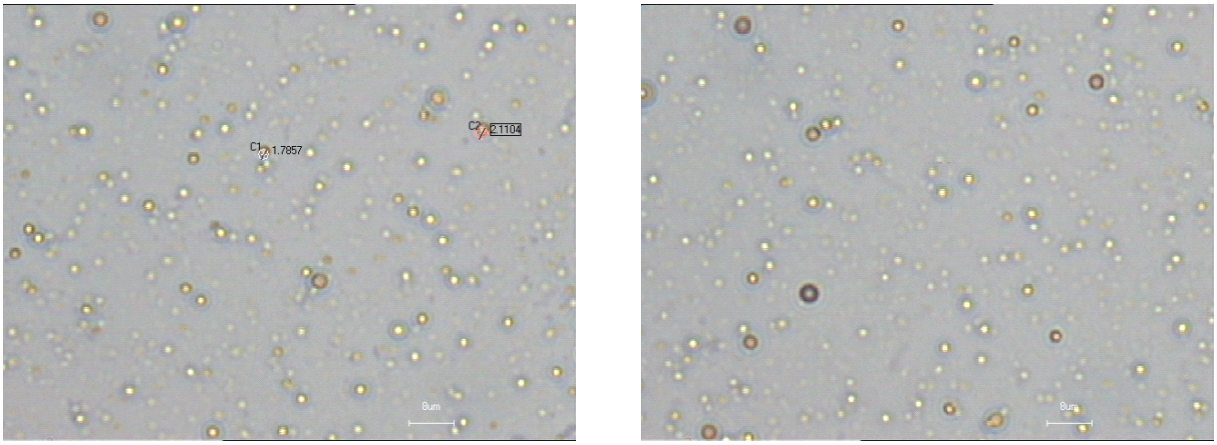


Fig.1 The microscope picture of crosslinker microcapsule

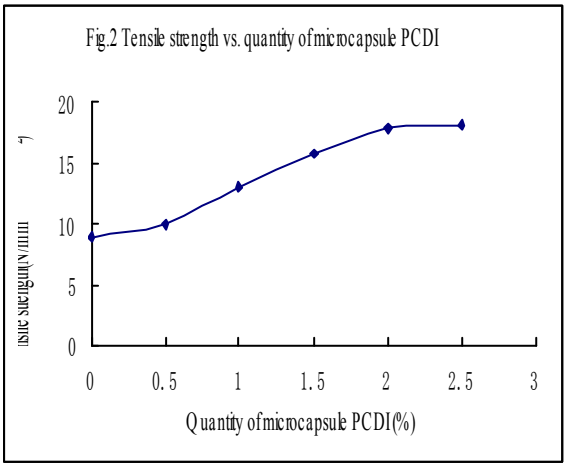
5 Applications

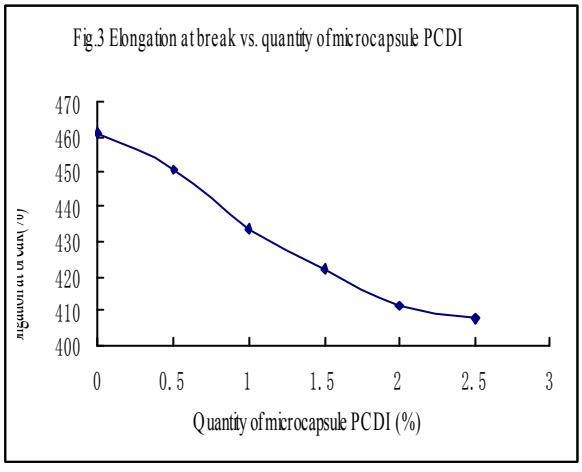
5.1 Mechanism and swelling ration of film

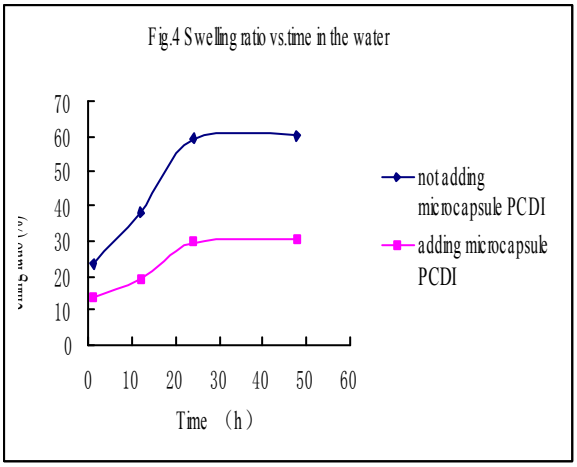
Polyurethane finishing agent (made in our laboratory, the weight content of carboxyl group was 4%) and 2% (calculate by the pCDI) pCDI microcapsule were mixed and formed film at 80℃. The thickness was about 0.5mm. The film was treated by the ironing machine (temperature: 80℃, pressure: 100kg/cm²). The mechanism and the swelling ratio of the film were studied. The tensile strength and elongation at break were tested with different quantity of microcapsule pCDI. The swelling ratio of film in alcohol and water were tested.

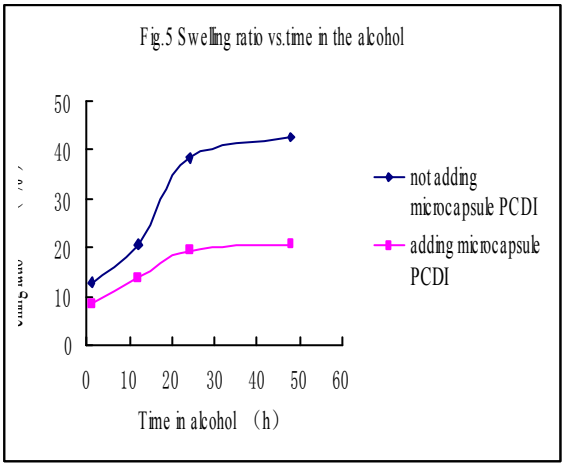
Fig.2 and Fig.3 show that with increasing quantity of microcapsule pCDI, the tensile strength was increased and the elongation at break was decreased. When the quantity of pCDI was more than 2%, the tensile strength increase little.

Fig.4 shows compare with not adding microcapsule pCDI, the swelling ratio of adding was better. The same situation happened in the alcohol (fig.5). It indicated the film can get better swelling ratio in the water and alcohol after using the microcapsule pCDI.









5.2 Storage stability of microcapsule PCDI

The microcapsule pCDI and waterborne pCDI (made in our laboratory) dispersion were stored in closed vessel without nitrogen, observing separately the breaking time and gel time.

Tab.5 shows the microcapsule PCDI has better storage stability.

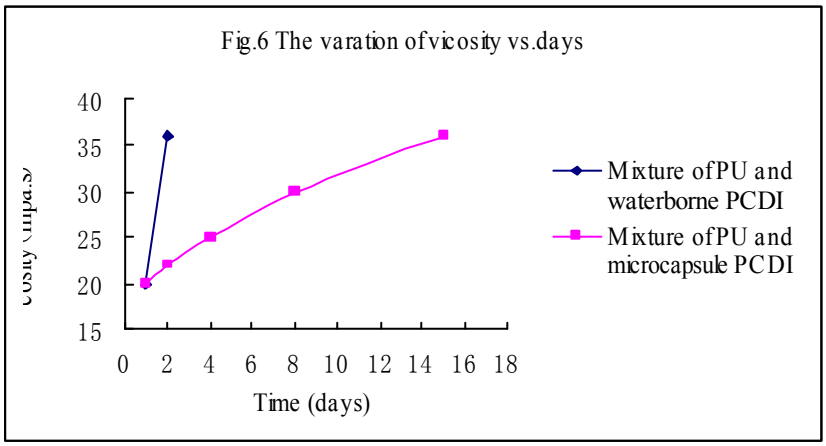
Tab.5 the storage stability of microcapsule pCDI and waterborne pCDI

	Microcapsule pCDI	Waterborne pCDI
Storage stablity	6 months	3 months

5.3 Pot-life of mixture of PU and microcapsule p *CDI*

The viscosity about the mixture of polyurethane finishing agent and waterborne pCDI and the mixture of polyurethane and microcapsule pCDI were tested by the rotary viscosimeter in different days (Fig.6).

Fig. 6 shows the pot life of the mixture of PU and waterborne pCDI was only 2days. But the pot life of mixture of PU and microcapsule pCDI prolonged to 15 days.



6 Conclusions

In this synthesis, hydrophobic carbodiimide crosslinker was chosen as core material and the reaction product of HDI and diethylenetriamine was chosen as wall material. A preferred synthesis process was given as follow: phase weight ratio=8:1, core and wall material weight ratio=40:1, the reaction product of HDI and diethylenetriamine was chosen as wall material. The microcapsule size was 1～3μm, the microcapsule air tightness was 1.08%. The application of microcapsule pCDI showed the tensile strength was increased and the elongation at break was decreased, the microcapsule pCDI has better storage stability and the pot life of mixture of PU and microcapsule pCDI was prolonged.

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