Paper B45

Performance & characterization of caprolactam-butylacrylate co-modified casein(CA-CPL-BA) leather finishing agent prepared from emulsifier- free emulsion polymerizaiton

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Abstract

For the purpose of gaining a better understanding of the way caprolactam-butylacrylate co-modifying casein (CA-CPL-BA), we studied performance and micro structure of CA-CPL-BA leather finishing agent prepared from emulsifier-free emulsion reaction. Through the performance study, effects of initiator species and dosage were detected, respectively. Results showed that when 5% KPS+$NaHSO_3$ was applied as the initiator, grafting extent of the monomers and film properties reached optimum. CA-CPL-BA was applied in leather finishing process and the mechanical properties of finished leather samples were tested. Results showed that the flexing resistance of leather samples finished by CA-CPL-BA was poorer while the strength tensile was better than that finished by the similar commercial product. Color developing ability of CA-CPL-BA was affirmed poorer than caprolactam modified casein(CA-CPL) by color measuring and matching system. Hydrophobic property of CA-CPL-BA film was confirmed preferable than CA-CPL and pure CA by contact angle test. Transmission electron microscope (TEM) and Dynamic light scattering (DLS) results demonstrated that emulsifier-free emulsion polymerization had taken place, and the latex particle size and corresponding PDI of CA-CPL-BA was smaller comparing to that of CA-CPL.

1. Introduction

Due to the decline in available fossil resources and the increasing preference toward environmentally friendly plastics, biodegradable and biocompatible polymers have received considerable attention from both academic and industrial researchers over the past decade [1-4]. The current generation of biobased polymers are produced primarily from renewable resources, such as sugar cane, proteins, and starches; such materials for packaging, adhesives, coatings, and biomedical applications can be produced with less overall energy consumption than their petrochemical counterparts and tend to be less toxic to the environment.

Casein, of which chemical composition is $N_{170}H_{268}N_{42}SPO_{51}$, is a type of natural protein extracted from

non-fat milk. As a natural polymer, it is a completely biodegradable and reproducible raw material and has certain film-forming properties as well as good adhesive force, strong resistance to ironing, grazing and high-temperature. However, casein film has less extensibility and water resistance and becomes mildewy and crazing easily due to its structure[5], which might restrict its practical applications. Chemical modification of the casein structure or blending with other materials, including plasticizers[6], cross-linkers[7],waxes[8], polymers[9] and nano-particles[10] have been attempted to correct its deficiencies. At present, modified casein is widely used as a film binding component of the paint, so it has a wide range of applications fields such as in papermaking, printing, coating, leather finishing and other industries [11-15].

In recent years, more and more attention has been paid on emulsifer-free emusion polymerization. Emulsifer-free emusion polymerization refers to the reaction completely without emulsifier or only with traces of emulsifier (concentration less than the Critical Micelle Concentration) during the emulsion polymerization process. Comparing with the conventional emulsion polymerization, negative phenomena including water-absorption and transfer of emulsifiers could be avoided. Consequently, the emulsifer-free emusion could be granted superior performances besides environmental function[16].

In our previous study, certain researches have been done on modifying casein including preparing caprolactam modified casein(CA-CPL) leather finishing agent from casein and caprolactam[17-19]. However, CA-CPL had some defects needed to be improved such as water resistance and flexibility given to leather. Butylacrylate (BA) is proved to be an excellent vinyl monomer which can help making up those defections. This paper aims at preparing caprolactam-butylacrylate co-modified casein(CA-CPL-BA) through emulsifer-free emusion reaction, studying its performance as well as the micro-structure.

2. Materials and method

2.1 Materials

Casein was purchased from Zhejiang Huatian Ltd. Triethanolamine was purchased from Tianjin Fuyu chemical engineering Ltd. Caprolactam was purchased from Shanghai Guoyao chemical reagents Ltd. Acrylic esters were purchased from Tianjin kemio chemical reagents Ltd. Acetone and N, N'-dimethylformamide (DMF) were purchased from Tianjin Bodi chemical Ltd.

2.2 Preparation of CA-CPL-BA

A certain amount of casein and alkaline solution were added into a 250 mL three necked flask fitted with a precision electric stirrer, a reflux condenser, a thermometer and two constant pressure dropping funnels. Kept stirring 1h after casein reached completely dissolved under 65ºC. Heated it up to a certain temperature and dropwise added the dissolved caprolactam solution keeping reaction for 0.5h then heated it up to a certain temperature and the reaction was allowed 2h, added 1/3 of the initiator

solution, after stirring for 0.5h, put BA and 1/3 of the initiator in a constant pressure dropping funnel respectively and adjusted the dropping speed to make sure that they go into the system evenly at one time, carried on reaction for certain time, then added the remaining initiator before stirring for certain hours, after it cooled naturally, CA-CPL-BA was obtained.

2.3 Grafting percentage and grafting efficiency

A certain amount of obtained CA-CPL-BA was first extracted with 10% CH_3COOH aqueous solution(pH=2.9) , the obtained precipitation was then washed by ethanol, acetone and deionized water to move the unreacted monomers, initator and minor moleculars away. Weighed the precipitation after drying up ($m_{g+}m_h$). N, N'-dimethylformamide (DMF) was used for getting rid of the homopolymer and copolymer of monomers including P_{BA}, P_{CPL} and $P_{(BA\text{-}CPL)}$. Once dried up in vacuum drying ovens under 60□ after washing by deionized water(the whole extracting process lasts for 24h), Finally, weight of the obtained product was recorded (m_g).

Grafting percentage (G): $G = \dfrac{m_g - m_1 \times w}{m_1 \times w} \times 100\%$

Grafting efficiency(E) : $E = \dfrac{m_g}{m_g + m_h} \times 100\%$

Note: In the above formulas, m_g means the mass of grafted monomers; m_h means the total mass of P_{BA}, P_{CPL} and $P_{(BA\text{-}CPL)}$; w means the mass fraction of casein in CA-CPL-BA.

2.4 Measurement of mechanical properties

According to standard ISO 3376-1976, mechanical properties mainly tensile strength and elongation at break of the casein films and leather samples finished were measured using an universal testing machine (AI-3000). Prior to analysis of the mechanical properties, the casein films and leather samples were conditioned under standard atmospheric conditions for 24 h.

2.5 Polishing property, softness, handle feel and flexibility

Polishing property, softness, handle feel and flexibility of leather samples were evaluated by some experienced professional engineers through professional experiments, the results were recorded as + or ++.

2.6 Characterization

Prior to TEM and DLS analysis, the emulsion was diluted into 1% concentration by distilled water. TEM analysis was performed on a TEM instrument (H-600) while DLS analysis was carried out on a laser particle measuring instrument (BT9300Z); Films with certain thickness formed on the sheet glasses were observed through Optics Contact Angle Surveying Instrument (OCA 20); Color

developing ability testing were conducted on a computer color measuring and matching system (SF600) by measuring the K/S value of color finished.

3. Results and discussion

3.1 Effects of initiator species on performance of CA-CPL-BA

Potassium persulfate (KPS), ammonium persulfate (APS), their oxidation-reduction systems (KPS+$NaHSO_3$, APS+$NaHSO_3$) and azo initiator (AIBN) were used as the initiator, respectively. Effects of initiator species on performance of CA-CPL-BA including grafting percentage and grafting efficiency as well as mechanical properties of the films were inspected.

As we see, grafting percentage and grafting efficiency varied greatly because of different initiators used. The main reasons lie in that: the initiator is one of the most important factors influencing the polymerization. Different initiators exhibit different initiating capacities and diverse optimal initiating conditions. As shown in figure 1, the oxidation-reduction initiators (KPS+$NaHSO_3$, APS+$NaHSO_3$) showed better behaviors in polymerization than the oxidation systems (KPS, APS) as well as AIBN. That might because $NaHSO_3$ could reduce the activation energy of KPS and APS to some extent. Meanwhile, it is clear that grafting extent reached higher when KPS+$NaHSO_3$ was used than APS+$NaHSO_3$. Since when KPS+$NaHSO_3$ was used, the initiator system could bring about relatively more active monomer radicals taking part in the grafting reaction.

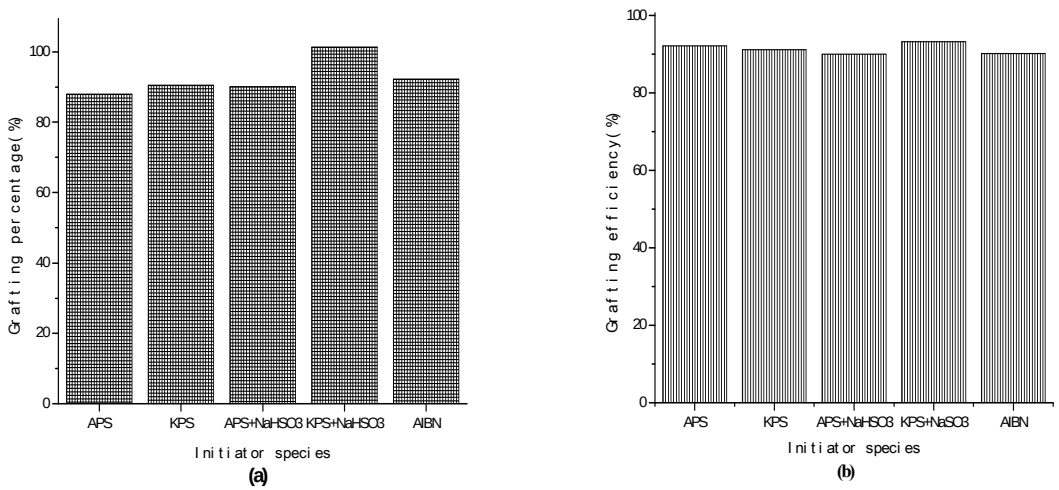

Figure 1.Effects of initiator species on grafting percentage (a) and grafting efficiency(b) of CA-CPL-BA

Having seen in figure 2, we can draw a conclusion that when KPS+$NaHSO_3$ was applied in initiating, the film had the most excellent flexibility (elongation at break) while the tensile strength was relatively poorer. This result was consistent with what we obtained from figure 1, since the better grafting extent meant more BA soft chains grafted onto casein chain, resulting in superior

flexibility of the film. However, as we know, changing trend of elongation at break and tensile strength are not the same for most of time. And more BA chains onto casein might lead to reduced tensile strength.

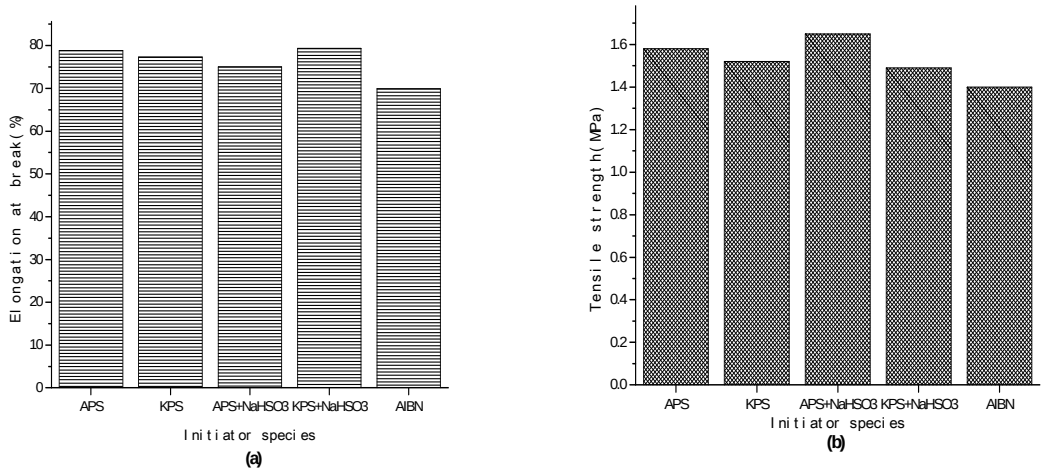

Figure 2 Effects of initiator species on elongation at break (a) and tensile strength (b) of films

3.2 Effects of KPS+$NaHSO_3$ dosage on performance of CA-CPL-BA

KPS+$NaHSO_3$ was applied as the initiator, in order to find out its optimal dosage for reaction, different amount of KPS+$NaHSO_3$ (1%-8%)were used and a series of emulsion were obtained. Effects of KPS+$NaHSO_3$ dosage on performance of CA-CPL-BA were studied by determining the characteristic of emulsion and films, results shown in figure 3.

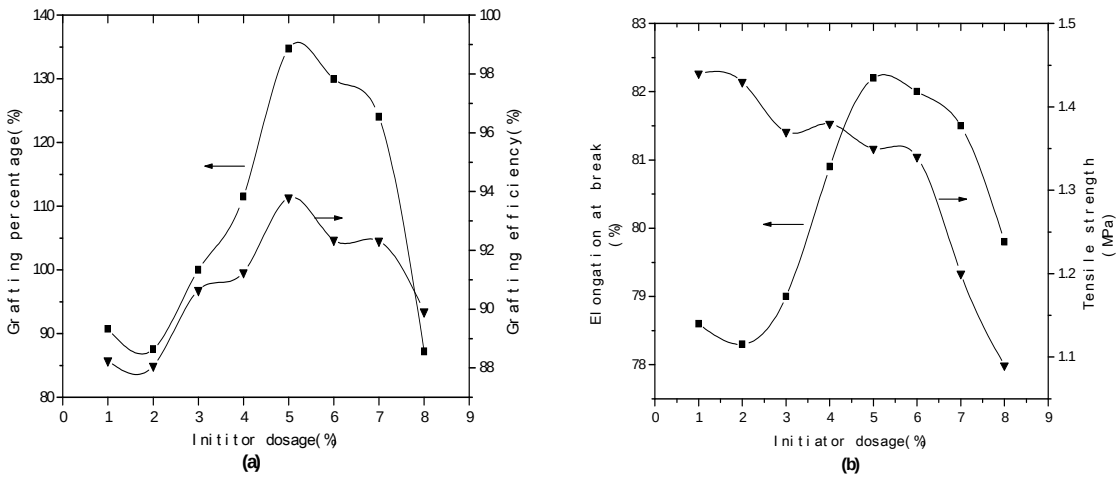

Figure 3 Effects of KPS+$NaHSO_3$ dosage on grafting extent (a) and mechanical performance of CA-CPL-BA film (b)

With regard to effects of KPS+$NaHSO_3$ dosage on grafting percentage and grafting efficiency of CA-CPL-BA, the results showed that: grafting percentage and grafting efficiency first increased then

decreased, and when 5% KPS+$NaHSO_3$ was used, the data reached the top points. Reasons might be that when the dosage of initiator was lower than 5%, the copolymerization proceeded more easily. So,the more initiator brought about more radicals, resulting in higher grafting extent onto casein. However, as the reaction proceeded, generating BA monomer radicals had been consumed gradually by grafting onto casein. This process wouldn't stop until the number of monomer radicals surpassed that of active groups on casein chains. Consequently, when the dosage of initiator was more than 5%, homopolymerization and copolymerization of modifying monomers win the grafting polymerization onto casein chain, resulting in the above phenomena. Meanwhile, when 5% KPS+$NaHSO_3$ was used, the elongation at break of films, standing for good flexibility achieved the most desired, it because that relatively longer BA chain had been grafted onto casein main chain.

3.3 Application Results

3.3.1 Mechanical properties of finished leather

In order to examine the application effects, the obtained optimal CA-CPL-BA was applied in leather finishing including undercoating, floating coating and top coating process, respectively. All the application results on leather samples finished by CA-CPL-BA were compared with that finished by the similar commercial product.

Table 1 Application results of CA-CPL-BA and similar commercial product

Performance of leather finished	Similar commercial product	CA-CPL-BA
Polishing property	+	++
Softness	+	++
Handle feel	+	++

(Note: "+" stands for good performance, "++"stands for the better.)

Judging from the application results in table 1 and figure 4, we could see that CA-CPL-BA gave better polishing property, softness, handle feel, flexibility to leather comparing to the similar commercial product. On the other hand, some defects still existed such as lower tensile strength, which needed to be improved in future researches.

3.3.2 Color developing ability

Color developing ability is a necessary performance for film-forming component in leather finishing agent. As is known to us, better color developing ability gives better compatibility between film-forming materials and colorants as well as superior application effects. Aiming at determining the color developing ability of the obtained emulsion (the film-forming material in finishing agent), color of finishing coatings was tested. In general, K/S value stands for the dark and light extent of color obtained. The high K/S value means the darker color as well as the high color developing ability. From the results seen in Figure 5, we can draw a conclusion that CA-CPL-BA exhibited the close color

developing ability to that of CA-CPL and CA. As we know, superior color developing ability requires excellent wetting and dispersing condition of colorants. Consequently, we could know that CA-CPL-BA had the desirable wetting and dispersing function to colorants, in spite of the increased hydrophobic ability than CA-CPL and CA.

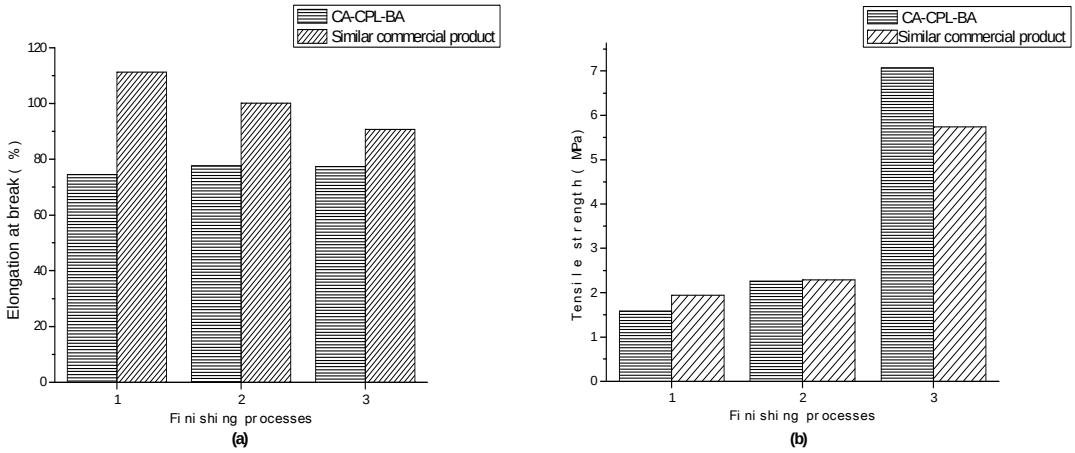

Figure 4 Elongation at break (a) and tensile strength (b) of finished leather

(Note: “1”,“2” ,“3” marked along the X axis refers to-undercoating, floating coating and top coating process ,respectively.)

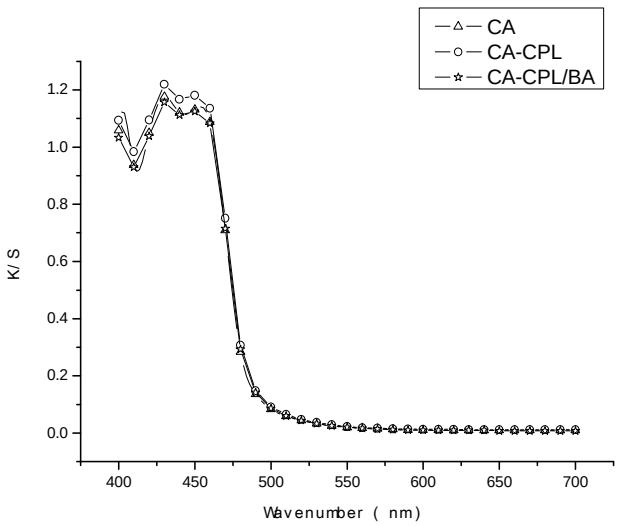

Figure 5 K/S value of coating colors

3.4 Detection &Characterization

3.4.1 Contact angle results

Table 2 Contact angle of film formed from CA, CA-CPL and CA-CPL-BA

Film formed from emulsion		Contact angle (°)
a	CA	23.6
b	CA-CPL	53.5
c	CA-CPL-BA	98.3

Contact angle value is a parameter indicating the wetting ability of liquids to solids. In our research, a larger contact angle value means a better wetting ability of water to the film. It is obvious shown in table 2 that the contact angle of CA-CPL-BA film was much higher that of CA and CA-CPL films. This could be easily explained by the fact of hydrophobic BA chains. Meanwhile, CA-CPL had slight stronger water resistance than pure casein had, which because the side chains became longer when CPL was introduced into the casein main chain.

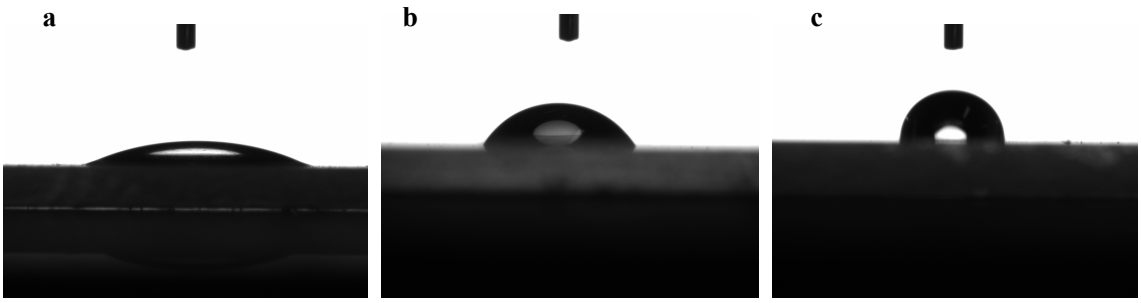

Figure 6 Contact angle images of film formed by CA, CA-CPL and CA-CPL-BA

3.3.2 TEM Results

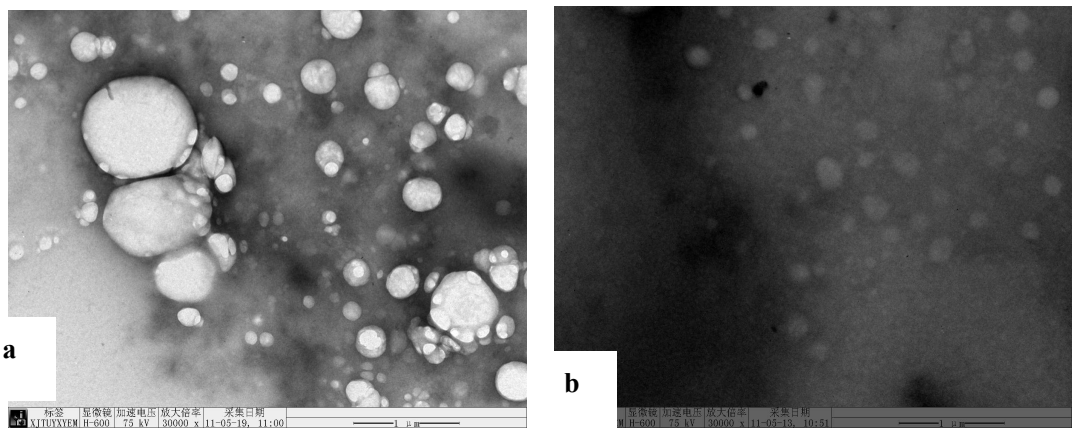

Figure 7 TEM images of CA-CPL(a) and CA-CPL-BA(b)(×30000)

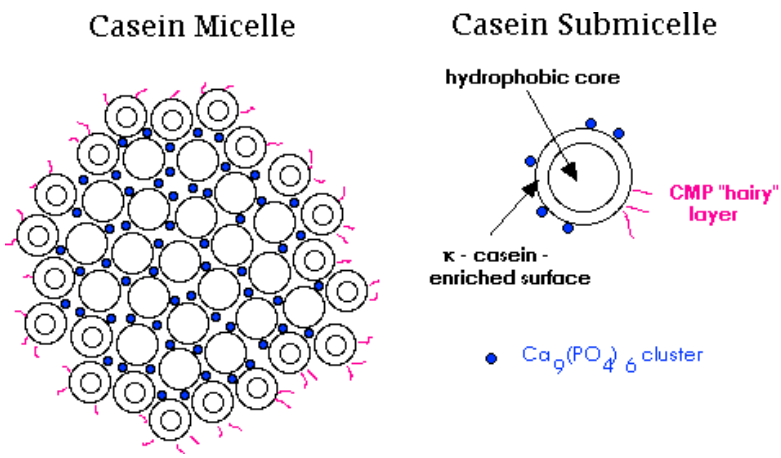

Figure 8 “casein sub-micelle” models

Seen from Figure 7, CA-CPL particle size varies from one to another, which can be explained that casein is a nature polymer, of which composition is complex. And through condensation reaction of casein and CPL, CA-CPL still kept the original structure by and large. Under this case, we can see the strawberry-like shape of CA-CPL particle which contains both casen micelle and submicelle. This could be elaborated with the help of “casein sub-micelle” model in figure 8. As we know, casein is a mixure composing of phosphoproteins. In its submicelle model, it is thought that there are small aggregates of whole casein, containing 10 to 100 casein molecules, called submicelles**.** The submicelles were linked by calcium phosphate. These submicelles contain a hydrophobic core and are covered by a hydrophilic coat which is at least partly comprised of the polar moieties of kappa-casein. The hydrophilic casein macropeptide (CMP) of the kappa-casein exists as a flexible hair, called “hairy layer”.

Comparing to CA-CPL particles, there were certain latex particles of relatively sphere shape in CA-CPL-BA , and the particle size was smaller and distributed more evenly, suggesting that linkage of calcium phosphate was destroyed and calcium phosphate was encapsulated into the micelles. Additionally, BA has reacted with active groups on casein chain by free-radical emulsifier-free polymerization, resulting in the uniform emulsion particles.

3.3.3 DLS Result

Table 3 DLS result of CA-CPL and CA-CPL-BA emulsion

Emulsion	Z-average size(nm)	PDI
CA-CPL	703.2	1.000
CA-CPL-BA	77.27	0.684

As shown in Table 3, the particle size of CA-CPL and PDI of CA-CPL-BA was smaller than that of CA-CPL. This could be explained that emulsifier-free emulsion polymerization did happen, which generated the even latex particle. The results of DLS were basically in agreement with those of TEM ,

which further demonstrated that BA has grafted onto casein chain and a nano-scale latex emulsion (CA-CPL-BA) obtained.

4. Conclusions

Caprolactam-butyl acrylate co-modified casein(CA-CPL-BA) leather finishing agent was successfully prepared from emulsifier- free emulsion reaction. When potassium persulfate and sodium bisulfite redox system (KPS+$NaHSO_3$) was used as the initiator, the grafting percentage and grafting efficiency reached highest than those initiated by other initiators. When 5% KPS+$NaHSO_3$ was used as the initiator, grafting percentage and grafting efficiency reached the highest. Comparing with the application result of the similar commercial product, elongation at break of leather samples finished by obtained CA-CPL-BA was poorer while the strength tensile was better. Color developing ability of CA-CPL-BA was affirmed poorer than CA-CPL and pure CA while hydrophobic property of CA-CPL-BA film was confirmed preferable than CA-CPL and pure CA by contact angle test. TEM and DLS results demonstrated that emulsifier-free emulsion reaction did take place, and the latex particle size and corresponding PDI of CA-CPL-BA was smaller comparing to that of CA-CPL. However, the distributions of latex particles need to be narrow down in further researches.

5. References

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