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Synthesis of Novel surfactants, its copolymer and applications in

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Abstract

The current study envisages on the synthesis of novel amphoteric surfactant, diethylamino-lauryl itaconate (DEALI) and amphiphilic copolymer based on Lauryl itaconate-Acrylic acid from reactive surfmer, Lauryl itaconate (LI). The present work explores the application of former as amphoteric fatliquor, DEALIFL and the later as polymeric retanning cum fatliquoring agent. Owing to amphoteric nature of DEALI, DEALI-FL treated leathers shown to have excellent dye brilliance and uniform distribution and

1.0 Introduction

Polymerizable surfactants, ‘surfmers’ are functional

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penetration on the leather. Further, the study investigates the polymerised fat to produce upper leathers with excellent light fastness, reduce fogging and minimize Cr (VI) a carcinogenic generation in leather. The novel concepts based on reactive surfmer and their application as leather auxiliaries, discussed in the current study provides the lead to the leather chemical industry to develop sustainable high performance fatliquors based on renewable sources.

Keywords:Reactive Surfactants, DEALI- diethylaminolauryl itaconate, Surfmer, Polymerized fat

compounds, gained significant attention over the years, owing to their reactivity, surface activity and polymerizability.1 Insertion of polymerizable group in a

surfactant molecule results in formation of ‘surfmers’. The factors that are important for effective performance are the reactivity of the polymerizable unit, its location and the solubility of the surfmer in aqueous medium, which inturn is governed by its critical micelle concentration.2

Amphoteric surfactants synthesized through polymerisable surfactant routes have attracted significant interest because of their extensive industrial applications, especially their use as fatliquors in leather processing. They show high emulsion stability to salts responsible for the hardness of water, as well as to alkali salts. In the fatliquoring of leather and skins, they give pleasantly soft, lardy and supple feel after thorough application to leather.3

Dye finishes are distinguished by evenness and brilliance. In the case of suede type leathers, a silky nap with an attracting scribing effect is obtained. Owing to their amphoteric character, the surfactants are compatible with cationic, anionic, and nonionic ingredients, enabling their formulation in fatliquor preparations.

DEALI, is prepared through the conjugate Michael addition of an amino group, diethyl amine to a polymerisable surfactant lauryl itaconate having -unsaturated carbonyl group. Lauryl itaconate is synthesized by the esterfication of lauryl alcohol and itaconic acid. Itaconic acid has been extensively studied with regard to its polymerization kinetics, role of bulky substituents, chain stiffness and glass-transition temperatures.4.5 Being a polymerisable dicarboxylic acid, it has the potential of being readily derivatized to generate polymerisable surfactants.

α, β

The amphiphilic copolymers for leather applications are of significant owing to increased demand for ecological leather, ecological fatliquors with good comprehensive properties.6 The amphiphilic acrylate copolymer containing both hydrophilic (carboxyl) and hydrophobic (long alkyl) groups is one of the main alternatives to

conventional fatliquors and retanning agents. They offer the benefit of providing the leather with desirable strength and aesthetic softness characteristics and filling while reducing the total consumption of syntan and fatliquor in the recipe substantially.

The conventional surfactants are anchored on the polymer emulsion particle surface by physical forces alone and, hence their adsorption-desorption equilibrium has a crucial role in governing the stability and other characteristics of latexes prepared using them. It is desirable therefore to have the surfactants covalently bound to the polymer latex for enhanced stability and performance. This can be used by using reactive surfactants, which become an integral part of the polymer during polymerization and would selectively reside on the surface of the latex providing it the requisite stability. The area of reactive surfactants has witnessed a surge of activity during the last decade, in part because of the combined efforts of many European laboratories.7-8

These polymerisable surfactants have extensive applications such as in synthetic rubbers, paints, adhesives, binders, additives in paper and textiles, impact modifiers, solid phase flocculants, rheological modifiers, solid phase supports in catalysis, diagnostic assays, cell separation, and drug delivery systems.9 In this work an attempt has been made to utilize these class of polymers in leather treatment applications and this conference paper is the combination of our two inhouse works10-11

2.0 Experimental

Lauryl alcohol, itaconic acid, para toluene sulphonic acid, sodium hydroxide, diethyl amine, Acrylic Acid were used as AR grade without any further purification. Vegetable oil, mineral oil, chloroparaffin sulfonate, neutralization agent were industrial grade products.

2.1 Experimental Methods

Stage I: Synthesis of amphoteric surfactant, Janardhanan et al, 2012.10

(a) Synthesis of Lauryl Itaconate polymerisable

anionic surfactant (LI) and

186g of lauryl alcohol was heated at 105ºC for 15 min. to remove moisture present if any, followed by

the addition of 130g of itaconic acid and 3.2g (1%) of para toluene sulphonic acid. The temperature of the oil bath was heated to 115 ± 5 º C and maintained for 4h. The drop in the acid value was checked to make sure that the reaction was completed. After the completion of the esterification, pH was adjusted to 8.0 using sodium hydroxide.

(b) Synthesis of Di Ethyl Amino Lauryl Itaconate

amphoteric surfactant (DEALI):

Figure 1. Synthetic approach for DEALI

Stage II: Preparation of fatliquor, DEALI-FL and its application:

(c) Synthesis and Characterization of Polymeric

Fatliquor:

Fatliquor was prepared by taking a mixture of vegetable oils (12.5%), mineral oil (10%), chloroparaffin sulfonate (22.5%), and DEALI (20%). The composition was adjusted to 100 % using water, and applied on wet blue cow leather after

The LI was slowly added to dimethyl amine at room temperature for 30 min. (LI: diethyl amine, 1:1). Reactants were stirred at 30-32ºC as a neat mixture for 5h. The chemical reactions and structures of LI and DEALI were depicted in Figure 1.

The synthetic preparation of polymeric fatliquor and its characterization was discussed in detail by Vijayabaskar et al.11

neutralization with dosage of 8% (w/w) and evaluated as single fatliquor.

2.2 Characterization Methods

The synthesis was followed by chemical methods like the measure of acid value, % water content and pH. Acid value and % water content were carried out as per IS:548:1964. pH and IEP were measured using precalibrated standard LAB INDIA make pH meter.

FT-IR spectrum was taken using KBr pellet on BRUKER, IFS, 66V FT-IR spectrometer. 1H NMR spectrum was taken using $CDCl_3$ as a solvent for esters and CD_3OD, as a solvent using JEOL GSX 400, NB FT NMR

spectrophotometer.

Surface tension and critical micelle concentration (CMC) were determined using KRUSS tensiometer K100 (KRUSS GmbH, Hamburg) at ambient temperature by ring balance method.

3.0 Results and discussion

Figure 2. FT-IR and NMR spectra of LI and DEALI, A. FT-IR spectra of LI, B. FT-IR spectra of

DEALI, C. NMR spectra of LI, D. NMR spectra of DEALI

From figure 2A and 2 B, the stretching at 947 and 866 cm-1 are characteristics peaks of LI due to the presence of aliphatic unsaturation of the type CH2=CHOCOR. When LI was reacted with diethylamine to form DEALI, the compound was converted as saturated surfactant, hence absence of peaks at 947 and 866 cm-1. The

3.1 Analytical characterization of surfactants

The preparation of DEALI was carried out in two steps. The first step was carried out at 115 ± 5ºC by checking the drop in acid value till it becomes consistent. The ester was neutralized to the pH of 8.0 using sodium Hydroxide. During the second step, reactants were maintained at 30-32 ºC for 5 hours. After the completion of the reaction, % water and pH were analysed as 18.0 and 12.5 respectively. Final pH adjusted to 7.0 using formic acid.

stretching at 1351 and 771 cm-1 due to the deformation of –C-N- C functional group in the DEALI, Figure 2B.

These results confirms the formation of adduct at á,âunsaturated carbonyl compound of LI resulted in the formation of amphoteric functional group in DEALI.

Common functional groups in LI and DEALI had same chemical shifts as illustrated in the figure 2 C and 2D. Shifts occurred in both LI and DEAL at 0.9, 1.28 and 4.1 ppm. Shifts at 0.9 and 1.28 ppm were due to the presence of SP3 hybridized protons (C-H’s) of saturated carbon atoms of lauryl (CH3 type) group of the surfactants. Shift at 4.1 ppm was due to the presence of ester group of type –(OCOR). This shift occurred due to oxygenated SP3

hybridized protons (C-H’s) of ester functional group.

Shift occurred in LI at 4.8 ppm, due the presence of protons of aliphatic unsaturation of the type (-CH2=CH-), which was a characteristic of LI. During the conversion

3.2 Surfactants properties

From the surface tension readings it was very clearly understood that the CMC value of the amphoteric surfactant is almost 10 folds lesser than that of other conventional anionic surfactants. The reason can be

3.3 Performance evaluation of DEALI-FL

Table 1– Organoleptic properties of Amphoteric surfactants *

Properties Amphoteric Fatliquor, DEALI-FL Softness 5.0 Touch 5.0 Dye brilliance and evenness Good Tensile Strength (Kg/cm2) 381.0 % Elongation 16.0 Bursting Strength (Kg/cm) No bursting Distension (mm) 12.0

to amphoteric surfactant, the double bond got saturated with the addition of nucleophile. Hence the shift at 4.8 ppm disappeared in DEALI.

From figure 2 D, DEALI, shifts occurred at 2.3 – 2.9 and 3.3 – 3.7 ppm. The former was due to the presence of the protons of a saturated carbon atom attached to nitrogen, of –C-N type. And the latter was due to the presence of functional group of –(+NR3) type. Since the mentioned groups attached to DEALI formed only after the reaction with diethylamine, the shifts were not observed in the spectra of LI.

From the results of the spectra, ester formation in the surfactant LI and the amine addition for the conversion to amphoteric group in DEALI were confirmed very clearly.

attributed to the chain length of the carbon atoms in the amphoteric, which resulted in increased hydrophobicity. As a result, the amphoteric had a tendency to aggregate and form a micelle in lower concentrations.

*Scale of grading: 1: Very Poor, 2: Poor, 3: Good, 4: Very Good and 5: Excellent

Owing to the higher surface activity of amphoteric surfactant and its solubility in aqueous medium, it is aiding to a stable fatliquor, resulting in a stable emulsion at a range of pH. The amphoteric fatliquor DEALI-FL shown to have excellent dye brilliance, evenness and Tensile strength characteristics on the leather. The possible reason is that higher emulsion stability which primarily depends of the surfactant activity aids penetrating of fat well

into the leather and splitting of fibers, resulting in better softness.12 Fatliquor with Higher tensile strength is due to the higher stability of the surfactant.

Leather softness is normally achieved by the addition of surfactants to aid appropriate emulsification for better penetration. The emulsion is broken within the fiber structure, either by the reactive surfactant interacting with the charged substrate or through protonation by solution pH reduction to change HLB balance.13 Stable emulsion of DEALI produced good absorption and increased the penetration. The surfactant DEALI besides having the property of being able to emulsify and disperse the fats and oils, possessed the capacity of binding to proteins through electrostatic and hydrophobic interactions.14

Softness and touch of the DEALI-FL treated leathers were better because of the presence of cationic nitrogen group, which makes leather fiber softer or helped the leather for good absorption of fatliquor. In addition, the formation of hydrogen bonding and ionic bonding and also

Table -1 Details on the leather Trials

TRIAL 1		TRIAL 2	
LHS	RHS	LHS	RHS
Polymeric Fatliquor	15	-	12	-
Fatliquor	-	5	-	5
Syntan	-	20	3	20

the molecular weight of the system had some effect on the performance. The carboxylic group of the amphoteric surfactant can form chelate ring with the chrome on the leather. As a result, it can exert a strong action on leather through its physical and chemical interactions with the collagen fiber. This implies that the crosslinking density of collagen fibers improves after tanning and that the carboxyl groups play an important role in the tanning process.

In addition to better performance towards softness and touch, we could observe a drastic difference in dye brilliance and evenness using DEALI-FL. The amphoteric surfactant present in DEALI-FL improved the surface dye colour yield and evenness because the cationic group of DEALI can attract anionic dyestuffs through electrostatic coupling.15

3.4 Performance Evaluation of Polymeric Fatliquor

The polymeric fatliquor synthesized using copolymerization of LI and acrylic acid at selective ratio has been evaluated with less amount of syntans and other conventional fatliquors and compared to standard recipe of known percentages of conventional syntans and fatliquors to make upper type of leather, as shown in Table 1. In Trial 1 Polymeric fatliquor alone is used and compared with recipe of conventional process to make upper leathers. The physical and organoleptic properties are given Table 2 &3.

Tensile Strength (Kg/cm2)	256.25	218.9	244.78	220.89
Elongation(mm)	71	51	65	48
Grain Crack Load (Kg)	39	24	32	26
Distension 1	11.75	10.1	9.60	8.5
Bursting Load (Kg)	>65	32	>58	34
Distension 2	>12.28	11.30	>11.50	10.58

Table -2 Physical Properties

Lightfastness Grade 4 on grey scale	

Table -3 Organoleptic Properties

Inner softness	3.5	4.5	3.8	4.5
Fullness	4.0	4.5	4.0	4.5
Surface touch	4.5	4.5	4.5	4.5
Grain tightness	4.5	4.5	4.5	4.5
Feel	Slightly			

Leathery Slightly

papery

The slight papery feel could be adjusted by incorporation of little % of conventional fatliuquor in the recipe. We have launched fatliquors with surfmers as co surfactants and in the process of commercializing a retan fatliquor with both filling and to provide softness to leather.

4 Conclusion

The present study explores the synthetic preparation and application of sustainable fatliquoring agents based on renewable sources. The anionic surfmer, polymerisable surfactant, Lauryl Itaconate (LI) was synthesized. This was further reacted to diethyl amine to form amphoteric surfactant Di Ethyl Amino Lauryl Itaconate (DEALI). Based on this, amphoteric fatliquor DEALI- FL was prepared. LI and DEALI were characterized by FT-IR and 1H NMR spectra. The perfroamnce characteristics

Grade 3 on

Grade 4 on

Grade 3 on

grey scale

grey scale

grey scale

Leathery

papery

of leathers treated with DEALI were studied in detail. The leathers treated with DEALI-FL shown to have excellent penetration, thus physical strength properties. This is because of high surface activity and formation of stable emulsion over the pH range. Dye brilliance and evenness was better due to the presence of cationic group through electrostatic coupling with the anionic dyestuffs. Further, we extended the usage of LI to synthesize polymeric fatliquor with amphiphilic nature. This polymeric fatliquor functions both as a fatliquor and retanning agent matching the physical properties requirements of upper leathers. Apart from this, the light fastness imparted by this fatliquor could be taken as a major advantage. This also minimizes the loading of conventional fatliquors in the recipe which would result in fogging. The synthesis yields a better base for the development of high performance fatliquors for the leather industry.

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