Trade Science Inc.

August 2007 Volume 2 Issue 2

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ, 2(2), 2007 [50-55]

Study Of The Graft Modification Of Valonea Extract And Its Application In Leather Tanning

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Received: 20th April, 2007 ; Accepted: 25th April, 2007

ABSTRACT

The graft modification conditions of the valonea extract with acrylic monomers by graft co-polymerization method were studied. The structures of the tanning materials in valonea extract both before and after modification were characterized by FT-IR. The vertical section of leather tanned with different valonea extract at different tanning steps were examined by transmission electron microscope(TEM). The grain surface statuses of different leather were characterized by scan electron microscope(SEM). The properties of the modified valonea extract were investigated. The result showed that under the certain conditions, the modified product produced by the reaction of the graft co-polymerization possesses better physical properties and more excellent tanning properties than those of the unmodified valonea extract.

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KEYWORDS

Acrylic acid;
Valonea extract;
Graft co-polymerization.

INTRODUCTION

With the increasing of the environment protect consciousness, many people have paid their research attention to the studies of replacing chromium-tanning agents with vegetable tanning agents, so as to enlarge the application of extract and improve the environmental pollution[1-3]. As an excellent extract tanning agent, it should be pure, colorless and easy to dissolve. Above all, it should penetrate fast among the collagen fibers and combine with them firmly. At present, some extract tanning products in the market have lots of deficiencies, such as darkish color, slow penetration ability and making the leather rigidly. Thus, it is of great significance to modify the extract tanning agent to enlarge its application range and utilize the nature resources availably. One of the approaches to develop the properties of extract is to produce a modified extract with polymer. Ma He-wei et al[4] used Sulfonated lignin to modify the quebracho extract and found that the penetration rate of the modified extract was fast and the color of leather was light. Because of its excellent properties in terms of weatherablility and fullness and penetration ability, the polyacrylate material was often used to improve the properties of polymers[5,6], but its application in graft modification of the valonea extract was rarely reported. In this paper, we increased the

tanning properties of valonea extract by graft modification method with acrylic monomers and studied the optimal modification conditions and the leather properties tanned with the modified valonea extract. The structures of the tanning materials in valonea extract both before and after modification were characterized by FTIR. The vertical section of leather tanned with different valonea extract at different tanning steps were examined by transmission electron microscope(TEM). The grain surface statuses of different leather were characterized by scan electron microscope(SEM). The result shows that under the certain conditions, the modified product produced by the reaction of the graft co-polymerization possesses better physical properties and more excellent tanning properties than those of the unmodified valonea extract, which results from the long graft chains of polyacrylate in the modified valonea extract molecular, which could enwind within the peptide chains of collagen fiber and disperse the fiber and help to stabilize the inner structure of the collagen, so as to increase the mechanism properties of the leather.

EXPERIMENTAL

Materials

Valonea extract(industry product) was supplied by Shiquan extract plant,Shaanxi. Leather power was self-made in lab. Acrylic monomers were produced by Xi'an chemical plant. The other chemicals were laboratory reagents and were purchased from different manufacturers. And others were used as received.

Preparation of the graft modified valonea extract copolymer and acrylic monomers

Stoichiometric valonea extract, H_2O, $NaHSO_3$, organic acid and dispersant were added to a 250-mL, four-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a condenser, and a thermometer, and then the system was heated to 60-and stirred to dissolve the valonea extract for 30minutes. After that, $Na_2S_2O_8$, dissolved in water($Na_2S_2O_8$/water 1:10 w/w), was then added into the system at a lower temperature of 50- with stir. At the same time, Stoichiometric acrylic monomers such as acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, acrylamide and acrylonitrile were slowly dropped into the mixture at 60- within 90minutes, after 30minutes reaction, the modified valonea extract aqueous dispersions with a certain solid content were prepared. All the modified valonea extract aqueous dispersions were used to tan the acidic goatskin to gain the goat-leather and the increment of the leather shrink temperature(ΔTs) was measured.

Application of different valonea extract in tanning of the acidic goatskin

According to the technical parameters described elsewhere[7], in the symmetry parts of the acidic goatskin, several peaces of goatskin(20cmx15cm) were tanned by the valonea extract before and after modified to obtain the goat-leather, and the mechanical properties of the leather were tested after drying and finishing as usual.

Characterization

The Fourier transform infrared(FT-IR) spectra of the modified valonea extract was recorded with a Nicolet Magna IR 550 FTIR spectrometer at 25^{0}C. SEM and TEM photographs of the goat-leather tanned with the modified valonea extract aqueous dispersions were obtained by means of Cambridge S-250 and JEM-1200EXII type electron microscope respectively.The mechanical properties for all the goat-leather specimens were conducted on an Instron 4465 testing machine at a 50mm/min crosshead rate, and the specimens were made in accordance with GB1040-79(China).

The water-solubility component of the modified valonea extract aqueous dispersions was measured with the kaoline filtration method, and the filtrate was collected and dried in an evaporating dish at 100- in oven. The water-solubility component was calculated as follows:

Water-solubility component (%)

$$= \frac{w_1}{w_2} \times 100\% \quad (1)$$

where W_1 and W_2 are the weights of the residue in the evaporating dish and sample, respectively.

The content of tanning material and non-tanning material in the modified valonea extract aqueous dispersions were examined by means of tanning the chromic leather powder[8]. And the content of the non-tanning material can be expressed as follows:

Content of the non-tanning material(%)

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TABLE 1 : Effect of the monomers to the properties of the modified valonea extract

Sample	A_1	A_2	A_3	A_4	A_5	A_6
Monomer	Acrylic acid	Methyl acrylate	Ethyl acrylate	Butyl acrylate	Acrylamide	Acrylonitrile
Tanning material content %	50.32	49.21	48.56	47.98	39.25	41.63
ΔTs^0C	10	9.5	10	8.5	3	10

$$= \frac{G_1 \times 20 \times 1.2 \times (G_2 \times 20 \times 1.2 - 0.075)}{W} \times 100 \quad (2)$$

Where W is the weight of the modified valonea extract, G_1 is the residue weight of the off-tanning liquid for the modified valonea extract ample, while G_2 is the residue weight of the contrastive sample. So the content of the tanning material in the modified valonea extract can be expressed as follows:

Tanning material content(%)
= Water - solubility component(%) - Content of the non - tanning material(%) (3)

Other properties of the modified valonea extract and goat-leather tanned with the valonea extract were measured according to reference[8].

The increment of the leather shrink temperature (-Ts) was calculated as the formula:

Increment of the leather shrink temperature (ΔTs)=T_2-T_1 (4)

Where T_1 and T_2 are the shrink temperature of the leather after and before tanning with the valonea extract aqueous dispersions.

RESULTS AND DISCUSSION

Exploration of the reaction conditions

The extract is a nature product with complicated component. Any condition, such as acid, base, salt, Heat and light can change its structure and property, so as to affect its content of the tanning material and its application. So in this paper we made the tanning material content and the ΔTs of the goat-leather tanned with the valonea extract as the performance target of the modified valonea extract product to determine the optimal modification conditions.

TABLE 1 showed the effect of the different acrylalic monomers to the properties of the modified valonea extract and its tanning property(ΔTs). From TABLE 1 we can see that properties of the valonea extract modified with other monomers are the same approximately except for acrylamide and acrylonitrile. Because of the existence of ester bond, the homogeneous polymer of acrylate monomers can improve the softness of the leather and can be used as retanning agent. So the modification agent can be composed with the mixture of acrylic acid, methyl acrylate, ethyl acrylate and butyl acrylate, in which the acrylic acid is the main component.

TABLE 2 : Effect of the initiators to the properties of the modified valonea extract

Sample	B_1	B_2	B_3	B_4
Initiator	H_2O_2	$K_2S_2O_8$	H_2O_2-$NaHSO_3$	$K_2S_2O_8$-$NaHSO_3$
Tanning material content %	42.56	45.83	38.72	50.21
ΔTs^0C	7	9	2.5	12.5

TABLE 2 listed the properties of modified valonea extract and its tanning property (ΔTs) with different initiator. TABLE 2 showed that the sample initiating with $K_2S_2O_8$ TABLE 2. Effect of the initiators to the properties of the modified valonea extract.

$NaHSO_3$ redox initiator possesses an excellent property. Because the reductive agent can decrease the activation energy of the initiator and the modified reaction can carry out at a low temperature, so as to avoid the oxidation of extract at high temperature. So in this case the $K_2S_2O_8$- $NaHSO_3$ redox initiator should be the best initiator.

TABLE 3 showed the properties of modified valonea extract initiated with $K_2S_2O_8$–$NaHSO_3$ redox initiator and its tanning property (ΔTs) at different temperature. It can be seen that the suitable reaction temperature is at 50^0C.

TABLE 4 showed the properties of modified valonea extract initiated with $K_2S_2O_8$-$NaHSO_3$ redox initiator at 50^0C and its tanning property(ΔTs)

TABLE 3 : Effect of the reaction temperature to the properties of the modified valonea extract

Sample	C_1	C_2	C_3	C_4
Temperature(^0C)	40	50	60	70
Tanning material content	42.5	52.4	49.2	36.2
ΔTs^0C	7	12	9	0.5

TABLE 4 : Effect of the reaction time to the properties of the modified valonea extract

Sample	D_1	D_2	D_3	D_4	D_5
Tanning material content %	45.39	47.64	51.33	53.26	53.31
ΔTs^0C	8.5	9	12	11.5	12

TABLE 5 : Effect of the pH value to the properties of the modified valonea extract

Sample	E_1	E_2	E_3	E_4
Organicacid/ Monomers(w/w_1 %)	0.5	1	2	3
Tanning material content %	40.25	54.32	48.91	44.72
ΔTs^0C	1	12.5	8	9

TABLE 6 : Dispersity of monomers in the VTA-1 and its grafting efficiency

Index	Dispersity of monomers in the VTA-1 %			Grafting efficiency %
	Free monomers	Self-polymer	Copolymerizing with valonea extract	
Value	6.51	27.06	66.43	71.05

within different reaction time. TABLE 4 indicated that the properties of modified valonea extract could be improved by prolonging the reaction time to some extent. With most of the free radical consuming out, properties of the modified valonea extract was steady-going after 150 minutes. So the suitable reaction time is about 150 minutes.

The pH value of the system is another important factor for the graft modification reaction. In this paper we adjusted the pH value of the system by adding organic acid. TABLE 5 showed the properties of modified valonea extract initiated with $K_2S_2O_8$-$NaHSO_3$ redox initiator at 50- for 150 minutes and its tanning property (-Ts) within different organic acid dosage. It can be seen that the modified valonea extract has the best property at the 1% organic acid dosage, indicating that this pH value is suitable for the graft copolymerization reaction.

The optimized experimental of the graft modification condition

On the base of the above exploration experimental, we took an ulterior step to optimize the graft modification condition with orthogonal design method[9]. The result indicated that the properties of the valonea extract enhanced appreciably by graft modification at the optimal conditions. And we prepared the modified valonea extract aqueous dispersion VTA-1 at the optimal conditions.

The method of measuring the grafting efficiency and free monomers in the product VTA-1 was according to reference[5]. The grafting efficiency is calculated as follows:

$$\text{Graftingefficiency}(\%) = \frac{M_1}{M_1 + M_2} \times 100 = \frac{M - M_2 - M_3}{M - M_3} \times 100 \quad (5)$$

Where M is the total monomers adding to the reaction system, M_1 is the monomers copolymerized with the valonea extract, M_2 is the selfpolymerizing monomers in the system, and M_3 is the free monomers in the system. The result of dispersity of monomers in the VTA-1 and its grafting efficiency was listed in TABLE 6. From TABLE 6 it can be seen that most of the monomers copolymerize with valonea extract to form graft copolymer, and some monomers still selfpolymerize to form their homopolymer. But this limited monomers copolymerized with valonea extract can improve the tanning property of the valonea extract. On the other hand, the homopolymer of acrylate monomers in the extract product could penetrate into the leather fiber easily to fill in the leather selectively, so as to increase the fullness and softness of the leather.

The modified valonea extract aqueous dispersion VTA-1 and the unmodified valonea extract was both extracted by N'N-dimethylformamide to obtain tanning materials. After drying in the vacuum oven and triturating, the structures of the tanning materials were characterized by FTIR. figure 1 showed the FTIR spectra of the tanning materials in valonea extract before and after graft modification. In these spectra, comparing with the unmodified valonea extract, there were three more peaks(with wave-number of 820cm^{-1}, 1100cm^{-1} and 1490cm^{-1}) in the curve of the modified valonea extract, which represent the absorption peaks in the molecular of acrylate. and the peak with wave-number of 1490cm^{-1} was the absorption peak of -CH_2- in acrylate molecular which do not exist in valonea extract molecular. So it can be confirmed that the acrylate molecular has been grafted into the valonea extract molecular.

TABLE 7 listed some physical properties of the valonea extract before and after graft modification.

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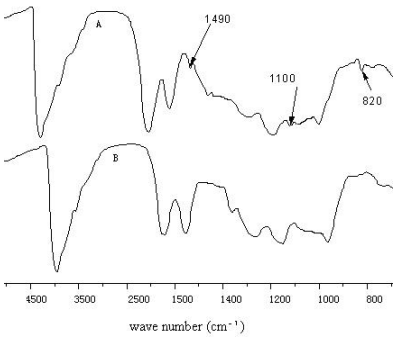


Figure 1 : FTIR spectra of the tanning materials in valonea extract before(B) and after(A) graft modification

TABLE 7 : Some physical properties of different valonea extract

Index	Valonea extract	Modified valonea extract
Solid content(%)	89.95	33.51
Water-solubility component(%)	77.07	96.21
Tanning material content(%)	43.25	57.43
pH value	3.82	3.20
Viscidity(cp·s)	1.6	0.9
Storage stability	Be musty after 7 days storage	Be unchanged more than 2 months
Salt-out value(ml)	10.25	19.40

TABLE 8 : Mechanical properties for the leather tanned with different valonea extract

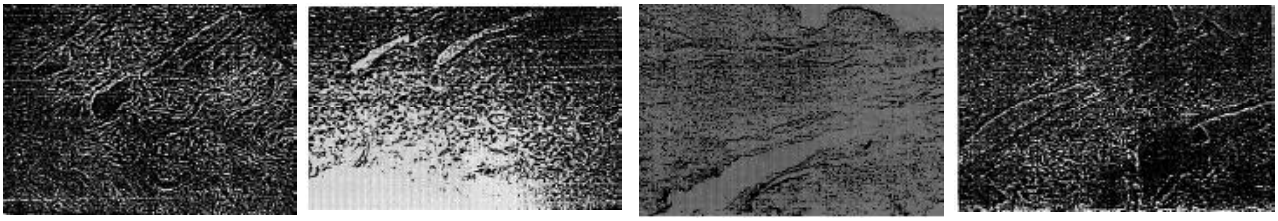
Index	Valonea extract	Modified valonea extract
Tanning time(h)	9	4
ΔTs(^{0}C)	9.5	17.5
Δb(%)	72	92
Tension strength(N/mm^2)	13.9	19.7
Extensibility(%)	25	34
Break-up height(mm)	8.5	10.3
Break-up strength(N/mm)	248	281
Tearing strength(N/mm)	34.7	47.1
Elongation at break(%)	63	79

From the results it can be seen that the modified valonea extract possesses more excellent physical properties than the un-modified one. Comparing with the un-modified valonea extract, the graft modification one possessed a high tanning material content, which was useful to increase the tanning property of the product. The increase of the water-solubility component after modification could be expected to solve the question of its dissolving at low temperature. And the enhancement of its salt-out value could be propitious to its penetration to the leather fiber. All of these improvements could help to enhance the tanning effect of the valonea extract and increase the quality of leather.

The mechanical properties for the leather tanned with the valonea extract before and after graft modification were measured and listed in TABLE 8. TABLE 8 showed that every mechanical properties of the leather tanned with the modified valonea extract were more excellent than that of the un-modified one. This obviously resulted from the long graft chains in the modified valonea extract molecular, which could enwind within the peptide chains of collagen fiber and disperse the fiber and help to stabilize the inner structure of the collagen, so as to increase the mechanism properties of the leather tanned with the modified valonea extract. Otherwise, it can be seen from TABLE 8 that the modified valonea extract penetrates faster than the unmodified one, indicating that the low molecular acrylate hemopolymer is helpful to speed the penetration of tanning agents into the leather fiber.

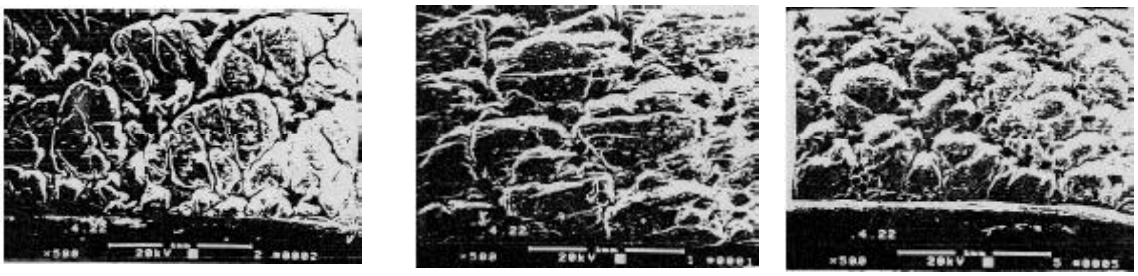
After embedding with glutin, fixing with formaldehyde, frost slicing-up and end capping, the vertical section of leather tanned with different valonea extract at different tanning steps were examined by transmission electron microscope(TEM) and shown in figure 2. Figure 2 showed that at the initial stages of tanning, the valonea extract was mainly penetrating among the leather fiber(1h) and primarily combining with leather fiber at the end of tanning process(4h). And the leather fiber clusters tanned with the modified valonea extract were much firmer and disperse better than that of the un-modified extract, that was why the fullness of the leather tanned with the former was better than that of the latter.

The grain surface statuses of different leather were characterized by scan electron microscope (SEM), As figure 3 showed because of the strong astringency of the valonea extract, the leather tanned with it would have a coarse grain surface(B), but after modifying with acrylate monomers, the astringency of the valonea extract decreased appreciably,



(A) : Tanned with un-modified valonea extract for 1h (B) : Tanned with un-modified valonea extract for 4h (C) : Tanned with modified valonea extract for 1h (D) : Tanned with modified valonea extract for 4h

Figure 2 : Tem photos of the vertical section of leather tanned with different valonea extract



(A) : The acidic goatskin (B) : Tanned with un-modified valonea extract (C) : Tanned with modified valonea extract

Figure 3 : SEM photos of the grain surface of leather before and after tanned with different valonea extract

and the leather tanned with it possessed an even grain surface(C).

CONCLUSIONS

A series of modified valonea extract aqueous dispersions were prepared to explore the optimal reaction conditions to obtain the best modification valonea extract product. And a graft modification valonea extract VTA-1 modified with acrylate monomers was prepared at the optimal reaction conditions and characterized. The experimental results show that the modified valonea extract possesses more excellent physical properties than the un-modified one. That is, the graft modification valonea extract VTA-1 has a high tanning material content, high water-solubility component content and excellent tanning properties, and it results from the long graft chains in the modified valonea extract molecular, which could enwind within the peptide chains of collagen fiber and disperse the fiber and help to stabilize the inner structure of the collagen, so as to increase the mechanism properties of the leather.

ACKNOWLEDGMENT

This work was financially supported by Jiangsu University advanced person bund (06JDG076) and Jiangsu Planned Projects for Postdoctoral Research Funds(0602037B).

REFERENCES

[1] F.X.Liang, X.Z.Yan, W.J.Wang; Leather science and engineering, **14**, 12-15 **(2004)**.
[2] J.G.Wang, Z.S.Yang, Z.Q.Zhao; China leather, **37**, 8-10 **(2006)**.
[3] Y.Chen, Y.J.He, B.Shi; Leather science and engineering, **12**, 18-21 **(2002)**.
[4] H.W.Ma, B.Shi; Leather Science and Engineering. **16**, 10-12 **(2006)**.
[5] Z.G.Huang, W.F.Shi; European Polymer Journal, **43**, 1302-1312 **(2007)**.
[6] E.P.Pedraza, M.D.Soucek; European Polymer Journal, **43**, 1530-1540 **(2007)**.
[7] J.G.Wang, Z.S.Yang, J.Z.Ma; China Leather, **31**, 1-5 **(2002)**.
[8] C.Z.Yu, X.L.Zhang; 'Leather analysis and testing', Light industry publishing company, **26-59**, **(1988)**.
[9] J.Luan; 'Optimal method of modern experimental design', Shanghai traffic university publishing company, **98**, **(1994)**.