

The Reaction Mechanism of Aldehyde-Acid Copolymer/MMT Nano-composite and Collagen Fibers

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Abstract: Aldehyde-acid copolymer/MMT nano-composite (P(MAA-AL)/MMT nano-composite) was prepared via monomer in-situ polymerization. Then the nano-composite was applied in leather tanning process and the leather structure after tanned was characterized by X-ray diffraction and Scanning Electron Microscope. The reaction mechanism between P(MAA-AL)/MMT nano-composite and collagen fibers was studied. P(MAA-AL)/MMT nano-composite has excellent dispersion property to collagen fibers. The tanning mechanism of P(MAA-AL)/MMT nano-composite is that the carboxyl groups of nano-composite combined to the amino groups of collagen side chains by electrovalent bonds and the aldehyde groups of nano-composite linked to the amino groups of collagen side chains by covalent bonds. The reaction activities for the active groups of polymer can be improved if nano-particles are properly incorporated. The tanning function of P(MAA-AL)/MMT nano-composite is the combination results of nano-particles and polymer. In the combined tanning process of P(MAA-AL)/MMT nano-composite and chrome tanning agent, P(MAA-AL)/MMT nano-composite is united with collagen by above manners firstly. Then the carboxyl groups of P(MAA-AL)/MMT nano-composite insert into the interior of chrome complex and coordinate with chrome. Crosslinking network is eventually formed between P(MAA-AL)/MMT nano-composite and chrome tanning agent and collagen fibers.

Key words: reaction mechanism; collagen fibers; nano-composite; aldehyde-acid copolymer

1 Introduction

Polymer modified with inorganic rigid particles, especially nano-particles is an optimum approach to achieve high performance and functional polymer materials¹⁻³. The introduction of nano-particles can not only efficiently enhance the mechanical properties, thermal and hydrothermal stability of polymer, but also impart unexpected functional characteristics such as UV-resistance, fungi-resistance, anti-radiation and water-resistance to polymer⁴⁻⁷. Nano-materials, due to its small size, plenty of un-pair-atom and high combination potentiality with polymer base, provide a possibility for application in leather tanning.

If nano-composite is formed by introducing inorganic nano-particles into polymer and then the nano-composite is imported into collagen fibers, the one is nano-combination can be formed between inorganic nano-particles and active groups of collagen fibers side chains, the other is the reaction activities for active groups in polymer side chains are enhanced by inorganic nano-particles, so the crosslinking between polymer and collagen fibers is accelerated. Therefore, the physical mechanical properties and hydrothermal stability of collagen fibers are improved and the aim of tanning is achieved. Meanwhile, the problem of chrome pollution existed many years in leather industry will be resolved⁸⁻⁹.

On this basis, in our study, aldehyde-acid copolymer/MMT nano-composite (P(MAA-AL)/MMT nano-composite) was prepared via in-situ polymerization. Then the nano-composite was applied in leather tanning process and the reaction mechanism between nano-composite and collagen fibers was studied.

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2 Experimental

2.1 Materials

Na⁺-montmorillonite (Na-MMT) was provided by Qing-he Chemical Factory, Zhangjiakou. Methacrylic acid (MAA), sodium hydroxide, isopropyl alcohol, sodium bisulphate and ammonium persulfate (APS) were all purchased from Tian-jin Chemical Reagent Factory. Acraldehyde (AL) was provided by Ke-long Chemical Plant, Chengdu.

2.2 Preparation of aldehyde-acid copolymer/MMT nano-composite

Na-MMT and deionized water were charged into a 250-mL 3-necked round bottom flask equipped with a reflux condenser, a thermometer and a magnetic stirring bar and stirred vigorously for 30 min. After MAA fed into the flask for 20 min, the mixture was treated with ultrasound for 20 min and stirred for 5 h at 60°C. Subsequently, the mixture was ultrasonically processed for 10 min. AL and sodium bisulphate were introduced into the mixture and stirred for 30min in the cool water bath, then the aqueous solution of APS and isopropyl alcohol were fed into the flask. The reaction was kept at 50°C for 3h.

2.3 Application of aldehyde-acid copolymer/MMT nan-composite

Self tanning: The leather samples were put into double weight sodium chloride solution (concentration 8%). The pH values of the solutions were adjusted to 5.5 using saleratus. 6% nano-composites were added into solutions and shaken for 6 hours. Then, the pH values of the solutions were adjusted to 3.5 using formic acid.

Combined tanning: The leather samples were put into double weight sodium chloride solution (concentration 8%). The pH values of the solutions were adjusted to 5.5 using saleratus. 6% nano-composites were added into solutions and shaken for 6 hours. Then, the pH values of the solutions were adjusted to 3.5 using formic acid. 2% chromate was added into solutions for 2 hours.

The weights of materials used were all based on leather weight.

2.4 Characterization

The X-ray Diffraction (XRD) patterns were obtained from a Japan Science 2200PC X-ray Diffractometer. The diffractograms were measured at 2 θ , in the range 2°-50°, using a Cu-K α incident beam ($\lambda=0.1546\text{nm}$), monochromated by a nickel filter. The scanning speed was 2°/min, and the voltage and current of the X-ray tubes were 40KV and 20mA, respectively.

The dispersion situation of collagen fiber was observed by Scanning Electron Microscopy (SEM).

The physical mechanical properties of leather were determined with GFU 55 Functional Materials Examination Machine made by Company (extending speed 100mm/min, backhaul speeding 100mm/min).

3 Results and discussions

3.1 The application results of aldehyde-acid copolymer/MMT nano-composite

Table 1 is the self tanning results of aldehyde-acid copolymer/MMT nano-composite. The shrinkage temperature of the leather tanned by P(MAA-AL)/MMT nano-composite was raised greatly and higher than that of the leather tanned by PMAA/MMT nano-composite. This indicates the electrovalence bond formed between carboxyl of nano-composite and amino groups of collagen fibers side chains (seen in Fig.1) is the main reason of hydrothermal stability of collagen improved by P(MAA-AL)/MMT nano-composite. Besides, aldehyde group also has positive contribution. The substance of interaction between aldehyde group of nano-composite and amino group of collagen fibers is a two step reaction of nucleophilic addition and β -elimination reaction. Schiff's base is generated eventually (seen in Fig.2) ¹⁰.

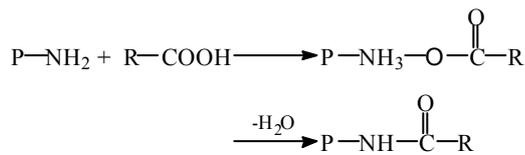


Fig.1 Sketch map of the reaction between carboxyl and amino group of collagen

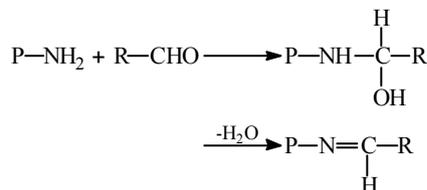


Fig.2 Sketch map of the reaction between aldehyde group and amino group of collagen

The shrinkage temperature increment of the leather tanned by P(MAA-AL)/MMT nano-composite was bigger than that of the leather tanned by P(MAA-AL). It shows when MMT are distributed evenly throughout polymer in the form of nano-layers, the reaction activities of active groups of polymer are boosted as greater specific surface ratio of nano-particles. The crosslinking between polymer and collagen is strengthened.

Tab. 1 The self tanning results

	ΔT_s (°C)	Thickness increment ratio (%)	Tensile strength (N/mm ²)	Tearing strength (N/mm)	Bursting strength (N/mm)	Elongation at break (%)	Elongation at unit load (%)
P(MAA-AL)/MMT nanocomposite	23	73.99	17.29	61.07	66.77	38.51	1.45
PMAA/MMT nanocomposite	21	71.13	22.06	58.36	67.00	45.92	6.78
P(MAA-AL)	20	56.07	15.40	41.97	62.50	39.29	1.61

The tensile strength is the load on cross section of the sample under longitudinal stretch. The tensile strength of leather samples varies with the compactness of collagen fiber weave, the angle of weave, the separation and the lubrication and the firmness of collagen fibers. The tearing strength is the largest load of the sample bearing when the crack again tears under unit condition. The tearing strength of leather samples varies with the compactness and the uniformity of collagen fiber weave. The bursting strength is the strength of the sample bearing force in all directions. The bursting strength of leather samples varies with the strength of the collagen fibers in the grain, the flexibility and the firmness of collagen fibers. In all, tensile strength and tearing strength both imply the flexibility of collagen fibers besides strength, while the bursting strength mainly concerns the flexibility of collagen fibers.

From Tab. 1, it can be known the tensile strength, tearing strength and bursting strength of leather tanned with P(MAA-AL)/MMT nano-composite were bigger than those of leather tanned with pure polymer. This adequately demonstrates the collagen can be simultaneously strengthened and toughened when nano-particles are properly incorporated into polymer.

At present, there are many explanations about strengthening and toughening mechanism of nano-

particles, such as physical and chemical interaction mechanism¹¹, tiny crazing mechanism¹², crack-crazing translation mechanism¹³, critical-thickness mechanism and physical crossing point mechanism¹⁴⁻¹⁵, etc. However, these mechanisms have some limitations because they are all aimed at some specific system. The strengthening and toughening mechanism accepted by most of researchers is made up of three reasons¹⁶. First, inorganic nano-particles can produce stress concentration phenomenon in deformation process. Matrix surrounding inorganic nano-particles yield and most of deformation work will be absorbed in this process. Hence, flexibility of materials is enhanced. Second, the inorganic nano-particles can not produce bigger elongation deformation. There is interfacial debonding between matrix and inorganic particles under great tensile stress in order that holes can be formed. Therefore, the expansion of crack can be blocked or the crack can be passivated. Meanwhile, the interfacial debonding and the yield caused by stress concentration need to consume much energy. Thus, flexibility of matrix is improved. Third, the greater specific area of nano-particles, the more physical and chemical defects on surface and the more chance of physical and chemical interaction between particles and polymer. So, the contact area of particles and matrix polymer become larger. It will give birth to much tiny crazing and absorb more impact energy when material suffers to impact.

Elongation at unit load and elongation at break of leather tanned with P(MAA-AL)/MMT nano-composite were decrease slightly compare with those of leather tanned with pure polymer. Elongation at unit load and elongation at break of leather samples have some relation with the softness of leather. Generally speaking, the higher the elongation at unit load and elongation at break of leather samples is, the softer the leather is. The elongation at unit load of leather samples is much smaller than the elongation at break. The elongation caused by unit load is mainly elastic deformation, so the elongation at unit load can be used to stand for the elasticity of leather to some extent. Therefore, the softness and elasticity of leather tanned with nano-composite were poorer than those of leather tanned with pure polymer. It is consistent with the report of literature³. This can be explained by noting that a dispersion of nano-sized particles allows the area of the interface with the matrix polymer to increase greatly, and therefore the polymer chains can be constrained more strongly. The ductility of matrix after added into MMT is decrease but the brittleness is increase.

Tab.2 The combined tanning results

Trial	T _s (°C)	Thickness increment ratio (%)	Tensile strength (N/mm ²)	Tearing strength (N/mm)	Bursting strength (N/mm)	Elongation at break (%)	Elongation at unit load (%)	Chrome content of waste liquids (mg/L)
1	91	93.86	17.69	69.12	64.29	40.92	8.93	120.43
2	69	73.99	17.29	61.07	66.77	38.51	1.45	—
3	75	53.14	16.48	41.12	43.02	51.24	20.44	319.81

1-the leather tanned with 6% P(MAA-AL)/MMT nano-composite associated with 2% chrome tanning agent; 2-the leather only tanned with 6% P(MAA-AL)/MMT nano-composite; 3-the leather only tanned with 2% chrome tanning agent.

Comparison between the physical mechanical properties of leather tanned with P(MAA-AL)/MMT nano-composite and those of leather tanned with PMAA/MMT nano-composite, the physical mechanical properties of leather tanned with nano-composite imported into aldehyde group descended. Generally, the defects of aldehyde leather are brittle, stiffness and lower physical mechanical properties. Therefore, it

again demonstrates there is really combination between the aldehyde group of P(MAA-AL)/MMT nano-composite and collagen fibers.

Tab. 2 shows the tanning results of P(MAA-AL)/MMT nano-composite associated with 2% chrome tanning agent. The shrinkage temperature, thickness increment ratio and mechanical strength of leather tanned with P(MAA-AL)/MMT nano-composite associated with 2% chrome tanning agent were higher than those of leather only tanned with 2% chrome tanning agent or 6% P(MAA-AL)/MMT nano-composite. Elongation were smaller than those of leather only tanned with 2% chrome tanning agent but increased significantly compared with those of leather only tanned with 6% P(MAA-AL)/MMT nano-composite. On the other hand, seen the chrome content of waste liquids, the absorbent ratio of chrome in float of P(MAA-AL)/MMT nano-composite and chrome tanning agent was higher than that of 2% chrome tanning agent. This may be because the carboxyl group of P(MAA-AL)/MMT nano-composite can be inserted into the interior of chrome complex and coordinate with chrome. Crosslinking network is formed between P(MAA-AL)/MMT nano-composite and chrome tanning agent and collagen fibers.

3.2 XRD analysis of leather

XRD pattern of leather tanned with 2% chrome tanning agent is seen in Fig.3. Two peaks on the left are the characteristic diffraction peaks of collagen fibers. The first peak is the distance peak of side chains. It represents the distance between complex helix chains of collagen. The second peak is the distance peak of skeletons and shows the distance of peptide chains. It is about 0.44nm. Two peaks on the right are due to the crosslinking between chrome tanning agent and collagen fibers.

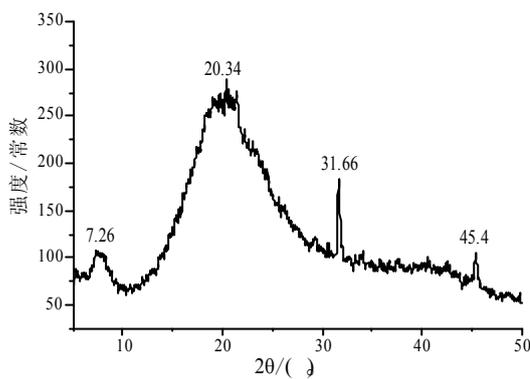


Fig.3 XRD pattern of leather tanned with 2% chrome tanning agent

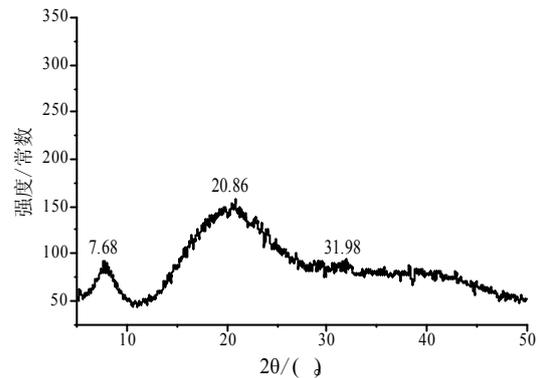


Fig.4 XRD pattern of leather tanned with P(MAA-AL)/MMT nano-composite and 2% chrome tanning agent

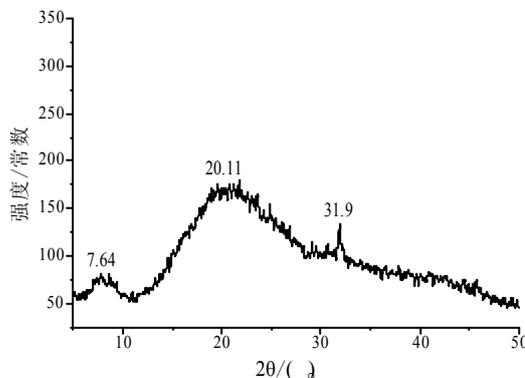


Fig.5 XRD pattern of leather tanned with P(MAA-AL) and 2% chrome tanning agent

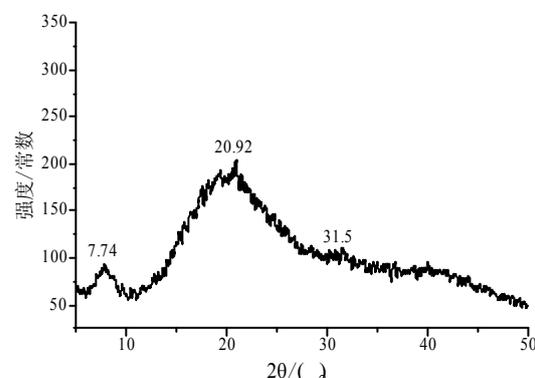


Fig.6 XRD pattern of leather tanned with PMAA/MMT nano-composite and 2% chrome tanning agent

Fig.4 is the XRD pattern of leather tanned with P(MAA-AL)/MMT nano-composite and chrome

tanning agent. Compared with XRD pattern of leather only tanned with 2% chrome tanning agent, the intensities of two characteristic diffraction peaks of collagen fibers were decrease and the positions of peaks displaced to bigger angle in Fig.4. At the same time, the two diffraction peaks due to crosslinking between chrome and collagen fibers became weaker. This indicates P(MAA-AL)/MMT nano-composite has excellent dispersion properties to collagen fibers. In tanning process, the combination is formed firstly between P(MAA-AL)/MMT nano-composite and collagen fibers. Then chrome and the carboxyl groups of nano-composite are linked by coordinate bonds and the crosslinking network is created at eventually.

The intensities of two diffraction peaks due to crosslinking between chrome and collagen fibers in Fig.4 were smaller than those in Fig.5. This represents the reaction activities of active groups of polymer after add in MMT can be enhanced and more combination is formed between polymer and collagen fibers. Hence, the coalescent of chrome and collagen fibers is counteracted. Most of chrome complex coordinates with carboxyl groups of polymer chains.

Compared with XRD pattern of leather tanned with PMAA/MMT nano-composite and chrome tanning agent, The intensities of two diffraction peaks of collagen tanned with P(MAA-AL)/MMT nano-composite and chrome tanning agent were decrease. Meanwhile, crystal degree of collagen fibers dropped from 10.14% to 6.74%. It is confirmed the combination of aldehyde group and collagen once again.

3.3 SEM analysis of leather

The SEM picture of leather tanned with P(MAA-AL)/MMT nano-composite and 2% chrome tanning agent is seen in Fig.7. The collagenous fiber bundles were small and dispersed uniformly and fibrils were much more. However, in the SEM picture of leather only tanned with 2% chrome tanning agent, the dispersion of collagenous fiber bundles was poor extremely and most of them had in the form of bigger fiber bundles. Single fibril was not seen. It indicates P(MAA-AL)/MMT nano-composite has good dispersion property to collagen.

Comparison of Fig.7, Fig.9 and Fig.10, the collagenous fiber bundles were smaller. Fibrils were more and distributed almost everywhere. This demonstrates the dispersion function of P(MAA-AL)/MMT nano-composite is superior distinctively to counterpart polymer and PMAA/MMT nano-composite.

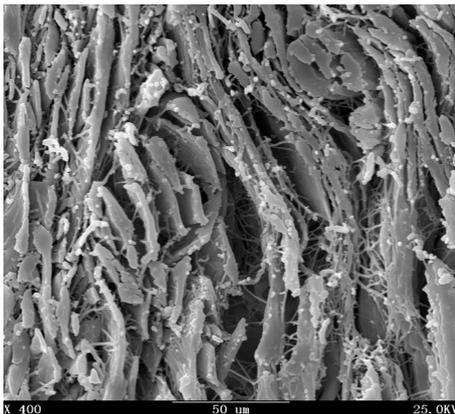


Fig.7 SEM picture of leather tanned with P(MAA-AL)/MMT nano-composite and 2% chrome tanning agent (×400)

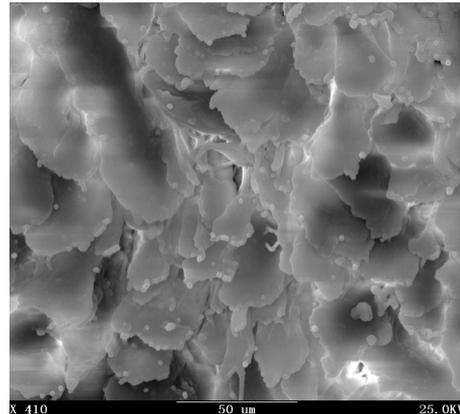


Fig.8 SEM picture of leather tanned with 2% chrome tanning agent (×400)

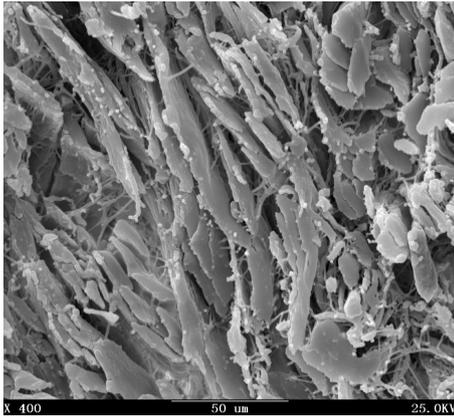


Fig.9 SEM picture of leather tanned with P(MAA-AL) and 2% chrome tanning agent (×400)

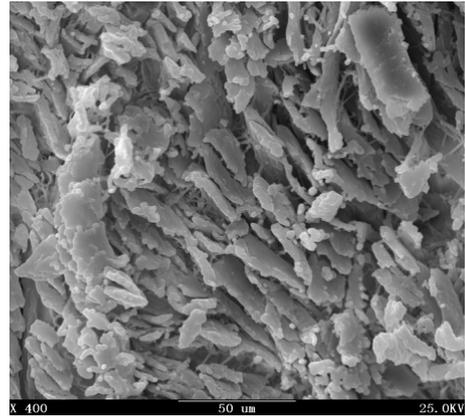


Fig.10 SEM picture of leather tanned with PMAA/MMT nano-composite and 2% chrome tanning agent (×400)

3.4 The tanning mechanism model of P(MAA-AL)/MMT nano-composite

Schiff's base is generated between the aldehyde group of P(MAA-AL)/MMT nano-composite and amino group of collagen side chains. The carboxyl of P(MAA-AL)/MMT nano-composite is combined with amino group of collagen side chains by electrovalent bond. Meanwhile, there accompany with many hydrogen bonds formed. The reaction activities of active groups of polymer can be improved when nano-particles are properly incorporated into them. The tanning function of P(MAA-AL)/MMT nano-composite is the combination results of nano-particles and polymer. It can be represented by the model of Fig. 11.

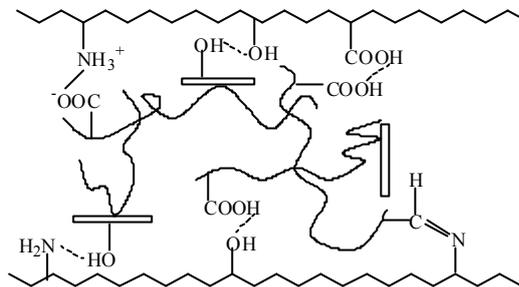


Fig.11 Tanning mechanism model of P(MAA-AL)/MMT nano-composite

In the combined tanning process of P(MAA-AL)/MMT nano-composite and chrome tanning agent, the active groups of nano-composite is combined with collagen fibers firstly. Then the chrome tanning agent coordinates with nano-composite. The crosslinking network is finally generated between chrome and nano-composite and collagen. The model of combined tanning mechanism is seen in Fig.12.

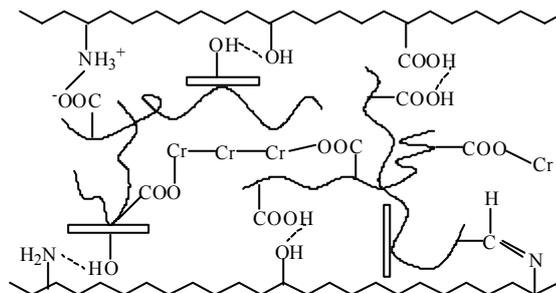


Fig.12 Tanning mechanism model of P(MAA-AL)/MMT nano-composite with chrome tanning agent

4 Conclusions

The hydrothermal stability, tensile strength, tearing strength and bursting strength of leather tanned with P(MAA-AL)/MMT nano-composite are increase but the elongation is decrease, Compared with those of leather tanned with pure polymer. The hydrothermal stability of leather tanned with P(MAA-AL)/MMT nano-composite and 2% chrome tanning agent can meet completely to the requirement. Moreover, P(MAA-AL)/MMT nano-composite is favorable to the absorption of chrome tanning agent. XRD and SEM analysis confirmed P(MAA-AL)/MMT nano-composite has excellent dispersion property to collagen fibers. The tanning mechanism of P(MAA-AL)/MMT nano-composite is that the carboxyl groups of nano-composite are combined with amino groups of collagen side chains by electrovalent bonds and the aldehyde groups of nano-composite are linked with amino groups of collagen side chains by covalent bonds. The reaction activities of active groups of polymer can be improved when nano-particles are properly incorporated into them. The tanning function of P(MAA-AL)/MMT nano-composite is the combination results of nano-particles and polymer. In the combined tanning process of P(MAA-AL)/MMT nano-composite and chrome tanning agent, P(MAA-AL)/MMT nano-composite is united with collagen by above manners firstly. Then the carboxyl groups of P(MAA-AL)/MMT nano-composite are inserted into the interior of chrome complex and coordinate with chrome. Crosslinking network is formed between P(MAA-AL)/MMT nano-composite and chrome tanning agent and collagen fibers at eventually.

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