Preparation of Nanocomposites Containing Montmorillonite and SiO_2 Particle for Leather Tanning Agent

by

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Abstract

Nanocomposites containing montmorillonite (layered silicate clay) and SiO_2 particle were prepared via in-situ polymerization. The effect of synthesis conditions, such as surfactant and SiO_2 content, on the application properties of nanocomposite were investigated in details. Nanocomposite, which used hexadecyl trimethyl ammonium chloride as the surfactant, had the best application properties. The incorporation of SiO_2 was favored for improvement of wet-heat resistance temperature of the leather, in contrast to the nanocomposite without SiO_2. Nanocomposite facilitate the absorption of chrome. Fourier transform infrared spectroscopy (FT-IR) spectrum demonstrated that methacrylic acid was polymerized in the montmorillonite inter-lamellar and nano-SiO_2 was completely copolymerized with methacrylic acid monomers. X-ray diffraction (XRD) results suggested that montmorillonite layers were exfoliated during the polymerization process.

Resumen

Nano-agregados conteniendo montmorillonita (Arcilla silícea estratificada) y partículas de SiO2 fueron preparados por polimerización en-situ. El efecto de las condiciones de la síntesis, tales como contenido del tensoactivo y SiO2, fueron detalladamente investigadas en términos de las propiedades de aplicación de los nano-agregados. Nano-agregados, que utilizaron hexadecil trimetil cloruro de amonio como tensoactivo, tuvieron las mejores propiedades de aplicación. La incorporación de SiO_2 fue favorecida por la mejora en la temperatura de la resistencia al calor en húmedo, en contraste con los nano-compuestos sin SiO2. Nano-compuestos facilitan la absorción del cromo. El espectro obtenido por Espectroscopía Infrarroja por Transformada de Fourier (FTIR) demuestra que el ácido metaacrílico fue polimerizado en la montmorillonita inter-laminar y nano-SiO2 fue completamente copolimerizado con monómeros del ácido metacrílico. Los resultados de la difracción de rayos X (XRD) sugieren que las capas de montmorillonita fueron exfoliadas durante el proceso de polimerización.

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Introduction

The tanning process converts the protein of the raw hide or skin into a stable material, which will not putrefy and is suitable for a wide variety of purposes. It is one the most of important processes in leather making. The choice of tanning material plays an important role in this process. Because using chrome tanning agent the leather could be endowed with the best performance like fullness, flexibility, and high shrinkage temperature and so on, chromate is used extensively in leather making. However, only about 70% chromate can be adsorbed by leather so a lot of chromate is still retained in the waste water, which may bring environment pollution. Moreover, chrome is a limited and nonrenewable resource. Developed new chrome-free tannages or improvements of the absorption of chrome are the main solutions to this problem.

Nanocomposites exhibit improved or even novel properties when compared to micro- and macro-composites.[1-4] Strong interfacial interactions between the nanoparticles and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of the virgin polymer.[5-10] Therefore, nanocomposites exhibit a good prospect of application in leather tanning. In Pan et al.[11] reactive nano-sized SiO_2 particles copolymerized with maleic anhydride and styrene by initiating with BPO in toluene. They reported that when nanocomposite was applied in leather making, the leather had the better quality than the leather retanned with pure polymer, due to the introduction of SiO_2 nanoparticles. In our previous papers,[12-13] acrylic resin/montmorillonite (AR/MMT) nanocomposites was prepared by in-situ polymerization. Whether the nanocomposites still have good tanning properties, when two kinds of nanomaterials with different forms, layered and particle are incorporated into the polymer matrix? Here nanocomposites containing montmorillonite and SiO_2 particle were prepared via in-situ polymerization. The influences of surfactant and SiO_2 contents on the application properties of nanocomposite in leather tanning were investigated.

Experimental

Materials

Montmorillonite (MMT) was provided by Qing-he Chemical Factory, Zhangjiakou. Methacrylic acid (MAA), isopropyl alcohol and ammonium persulfate (APS) were all purchased from Tian-jin Chemical Reagent Factory. Nano-SiO_2 (RNS-D) was purchased from He-nan nanomaterial engineering center.

Preparation of PMAA/ MMT/ SiO_2 Nanocomposite

0.86g MMT and 50g deionized water were charged into a 250-mL three-necked round bottom flask equipped with a reflux condenser, a thermometer and a magnetic stirring bar and stirred vigorously for 30 min. After 28.8g MAA, 1.15g surfactants and different amount of RNS-D fed into the flask for 30 min, the mixture was treated with ultrasound and stirred at 60°C. Subsequently, the mixture was ultrasonically processed for 20 min. The aqueous solution of APS and isopropyl alcohol (2.3g APS and 0.3g isopropyl alcohol dissolved in 20g distilled water) were fed into the flask. The reaction was kept at 80°C for 2.5h.

Characterization of PMAA/ MMT/ SiO_2 Nanocomposite

The X-ray Diffraction (XRD) patterns were obtained from Japan Science 2200PC X-ray Diffractometer. The diffractograms were measured at 2θ, in the range 2°-10°, using a Cu-Kα incident beam (λ=0.1543nm), monochromated by a nickel filter. The scanning speed was 1°/min, and the voltage and current of the X-ray tubes were 40KV and 20mA, respectively. The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on 5DX FTIR using KBr pellets.

Application of PMAA/ MMT/ SiO_2 Nanocomposite

The shaved pickled goat skins were put into double weight sodium chloride solution (concentration 8%). The pH values of the solutions were adjusted to 5.5 using a sodium bicarbonate solution (concentration 10%). 6% PMAA/ MMT/ SiO_2 nanocomposites were added into solutions and shaken for 6 hours. Then, the pH values of the solutions were adjusted to 3.5 using formic acid. The weights of materials used were all calculated based on leather weight.

Results and Discussion

The Mechanism of PMAA/ MMT/ SiO_2 Nanocomposite

Montmorillonite belongs to the same general family of 2:1 layered or phyllosilicates. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide.[14] The layer thickness is around 1nm. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery, which is about 1nm. Details regarding the structure for montmorillonite are provided in Fig.1. Montmorillonite is a natural precursor of nanomaterial, and it has strong hydrophilic.

The nano-SiO_2 used in our research is modified by r-Methacryloxy propyltrimethoxysilane as coupling agent. The vinyl groups are introduced onto surfaces of SiO_2. Its structure is seen in Fig.2. Hence, it is a hydrophobic material. The surfactant must be used if SiO_2 and montmorillonite come to the better compatible state.

The whole polymerization procedure of PMAA/ MMT/ SiO_2 nanocomposite includes both the free radical polymerization reaction and the intercalated reaction. MMT is dispersed sufficiently. Nano- SiO_2 and methacrylic acid are intercalated into the galleries of MMT. Then the nanocomposite materials

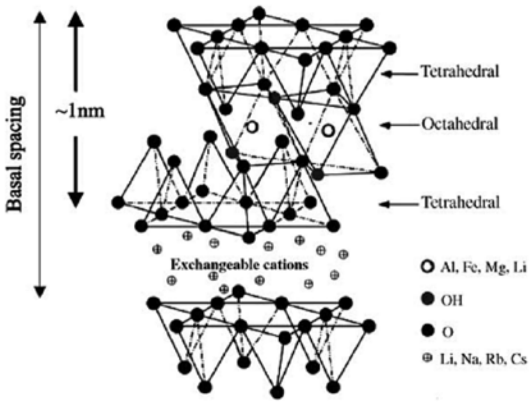

Figure 1. The structure of montmorillonite.

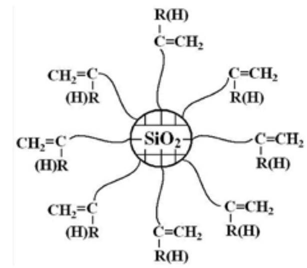

Figure 2. The structure of nano-SiO_2.

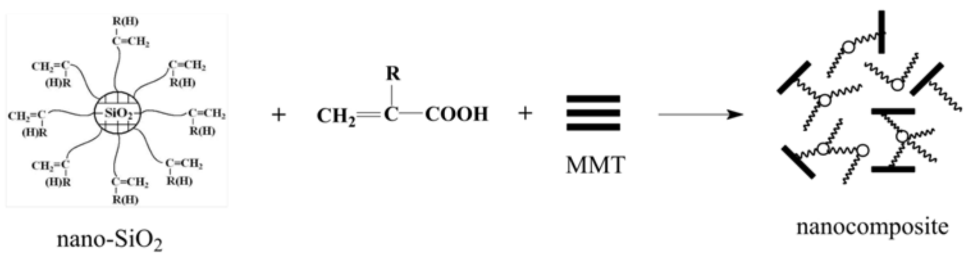

Figure 3. Reaction model of PMAA/MMT/SiO_2 nanocomposite.

are obtained by the polymerization between double bonds on the surface of SiO_2 nanoparticle and methacrylic acid. Fig.3 shows the reaction mechanism of PMAA/ MMT/ SiO_2 nanocomposite.

Effect of Surfactants

Table I is the application results of nanocomposites with different surfactants. The selective surfactants are all cationic surfactants. This based mainly on a concern for two points. The one is cationic surfactant can take place ion exchange reaction with cations between montmorillonite layers. So the interlayer spaces of montmorillonite increase. Monomer or SiO_2 can enter easily into montmorillonite interlayer and take place polymerization. The other is surfactant has certain emulsification. It can increase the compatibility of montmorillonite and SiO_2.

The wet-heat resistance temperature refers to the shrinkage temperature of leather in a certain heating medium. It reflects workability and stability of leather in wet and heat conditions.

TABLE I
The application properties of nanocomposites with different surfactants.

Surfactants	T_1/℃	T_2/℃	△Ts/℃	Thickness increment ratio/%
Hexadecyl trimethyl ammonium chloride	60.0	75.8	15.8	146.1
3-chloro-2-hydroxypropyl trimethyl ammonium chloride	64.7	70.5	5.8	61.1
Dodecyl dimethyl benzyl ammonium chloride	65.2	72.3	7.1	58.2
Octadecy trimethyl ammonium chloride	62.9	69.4	6.5	33.6
Dihexadecyl dimethyl ammonium chloride	63.5	71.1	7.6	61.8

Note: T_1 is the wet-heat resistance temperature of leather before tannage; T_2 is the wet-heat resistance temperature of leather after tannage; △T is the improvement of the wet-heat resistance temperature of leather after tannage.

Leather manufacturing processes, such as fatliquoring and dying, need to be carried out in water that often is heated. The processing of leather into leather products also often requires wetting and heating. Therefore, wet-heat resistance temperature is an important and basic test index of leather. When the wet-heat resistance temperature is high, the leather in wet and heat conditions is more stable. The thickness increment ratio demonstrates the extent of the thickness change of leather before and after chemical treatment. The thickness corresponds with the fullness of the leather. Generally, the wet-heat resistance temperature and the thickness increment ratio of leather are closely related to the crosslinking degree of collagen fiber. When the collagen is treated by nanocomposite, the carboxyl group of nanocomposite is combined with amino group of collagen side chains by electrovalent bond. Meanwhile, there is accompanied by many hydrogen bonds formed. Therefore, an interpenetrating network structure including intramolecular crosslinking and intermolecular crosslinking of collagen is formed. The reaction mechanism between nanocomposite and collagen is seen in Fig.4.

According to table I, the application properties of nanocomposite that used hexadecyl trimethyl ammonium chloride as surfactant are the best. The reason for this is that the chain lengths of all kinds of surfactants are different. It leads to the difference of intercalated effect. The chain length of surfactant is shorter, the change of the interlayer space of montmorillonite is smaller. However, if the chain length of surfactant is longer, it enters difficultly into montmorillonite interlayers and the intercalated effect is also bad. The structure of nanocomposite formed is different along with the difference of intercalated effect of montmorillonite. Hence, the application properties of nanocomposites are different. This consistent with the experimental results reported in the literature that montmorillonite modified by hexadecyl trimethyl ammonium chloride is the best.

Effect of SiO_2 contents

The influence of different SiO_2 contents on the application properties of the nanocomposite is shown in table II. The incorporation of SiO_2 results in the thickness increment ratio and the shrinkage temperature increase rapidly and then decreases. The application properties of nanocomposite without SiO_2 are the worst. This indicates SiO_2 has certain tanning properties. SiO_2 agglomerates easily and disperses unevenly along with SiO_2 contents increasing. Therefore, the application properties of nanocomposite containing more SiO_2 are the worse.

The Application Properties of PMAA/ MMT/ SiO_2 Nanocomposite

In order to study the absorption of PMAA/MMT/SiO_2 nanocomposite to chrome, 6% PMAA/MMT/SiO_2 nanocomposite-2% chromate combination tannage was applied on the shaved goat pickle skins and the chrome content of waste liquor was tested. Moreover, the comparison study was carried out between combination tannage and 2% standard chromate tannage. Table III is the comparison results. Chrome content of waste liquor of 6% PMAA/MMT/SiO_2 nanocomposite-2% chromate combination tannage is obviously higher than that of 2% chromate tannage. It demonstrates PMAA/MMT/SiO_2 nanocomposite can improve the absorption of chrome. This is because PMAA/MMT/SiO_2 nanocomposite contains many carboxyl groups and hydroxyl groups. These active groups can coordinate with chrome. The shrinkage temperature and thickness increment ratio of leather tanned with 6% PMAA/MMT/SiO_2 nanocomposite and 2% chromate are improved significantly than those of the leather tanned only with 2% chromate. This indicates PMAA/MMT/SiO_2 nanocomposite has tanning effect again.

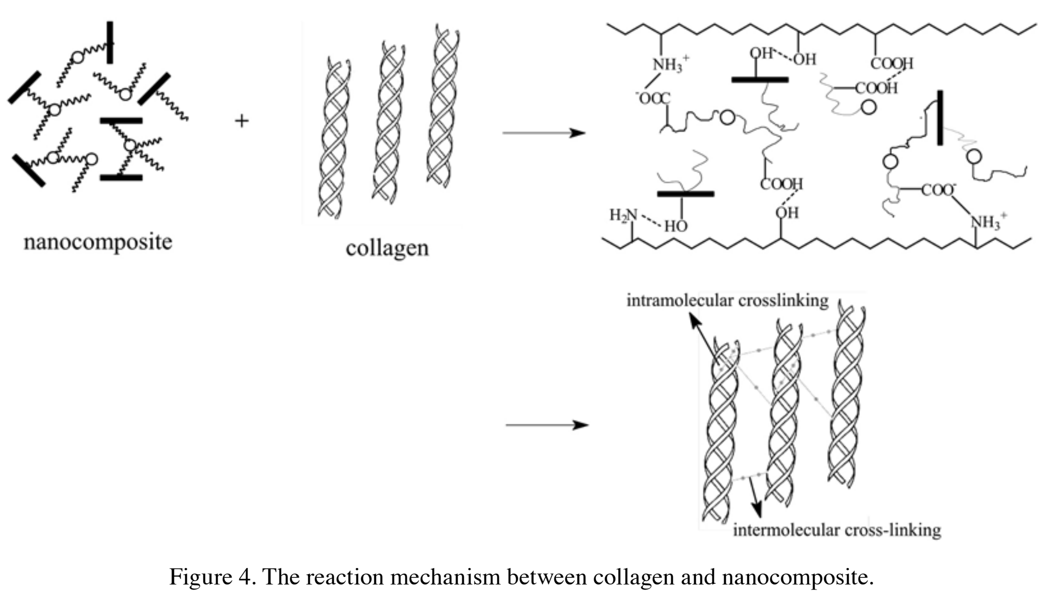

Figure 4. The reaction mechanism between collagen and nanocomposite.

TABLE II
The application properties of nanocomposite with different SiO_2 contents.

SiO_2 contents /%	T_1/°C	T_2/°C	△Ts/°C	Thickness increment ratio/%
0	52.3	69.4	17.1	87.9
1	44.7	71.1	26.4	100.2
2	43.7	67.0	26.9	100.5
3	44.1	67.0	22.3	90.3
4	43.5	65.2	21.1	89.5
5	41.1	62.3	18.8	91.0

Note: T_1 is the wet-heat resistance temperature of leather before tannage; T_2 is the wet-heat resistance temperature of leather after tannage; △T is the improvement of the wet-heat resistance temperature of leather after tannage.

TABLE III
The comparison results of tannage.

	Shrinkage temperature after tannage/°C	Thickness increment ratio/%	Chrome content of waste liquor/(mg/L)
6% PMAA/MMT/SiO_2 nanocomposite and 2% chromate	95.8	128.3	63.7
2% chromate	75	90.3	385.2

The Structure of Nanocomposite

Fig. 5 displays the differences among the structures of MMT, nano-SiO_2 and PMAA/MMT/SiO_2. The FT-IR spectrum of PMAA/MMT/SiO_2 shows that the intensity of the 3500–3200cm^{-1} band is increased. The -OH stretching frequencies are broadened and displaced to lower frequencies. These shifts are attributed to the formation of hydrogen bonds. On the other hand, the peaks at 2940cm^{-1} and 1490-1410cm^{-1} are ascribed to the vibration of methylene groups. The peaks at 1700cm^{-1} are due to the C=O stretching mode of carboxyl. These results show that methacrylic acid is polymerized in the MMT inter-lamellar. The absorption peak 1638cm^{-1} disappears, which explains that nano-SiO_2 is copolymerized with MAA monomers completely.

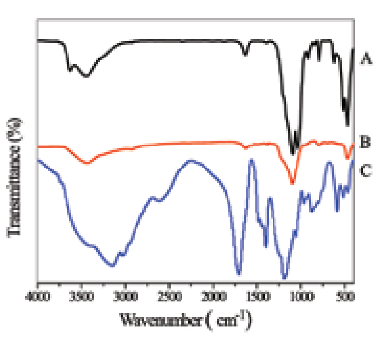

Figure 5. FT-IR spectra (A—MMT; B—nano-SiO_2; C—PMAA/MMT/SiO_2).

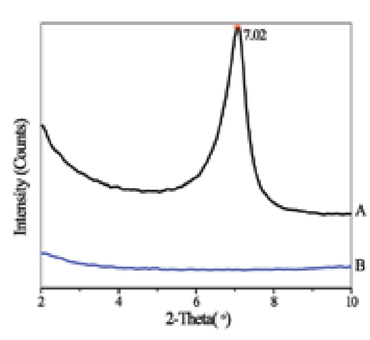

Figure 6. XRD patterns (A—MMT; B—PMAA/ MMT/ SiO_2).

Shown in Fig.6 are XRD diffraction patterns of pristine MMT and PMAA/MMT/SiO_2. A strong 001 characteristic diffraction peak of pristine MMT is appeared at the 2θ value 7.02° (curve A). Curve B gives typical XRD pattern of PMAA/MMT/SiO_2. The XRD results suggest that the MMT layers are exfoliated probably as indicated by the disappearance of the MMT diffraction peak in curve B. This is because the polymerization between double bonds on the surface of SiO_2 nanoparticle and methacrylic acid are taken place in the MMT interlayer.

CONCLUSIONS

The application properties of the PMAA/MMT/SiO_2 nanocomposite prepared via in-situ polymerization are strongly dependent upon the surfactant and SiO_2 contents. The application properties of nanocomposite that used hexadecyl trimethyl ammonium chloride as surfactant were the best. The incorporation of SiO_2 is favored for improvement of wet-heat resistance temperature of leather, in contrast to the nanocomposite without SiO_2. PMAA/MMT/SiO_2 nanocomposite facilitates the absorption of chrome. Fourier transform infrared spectroscopy (FT-IR) spectrum demonstrated that methacrylic acid is polymerized in the MMT inter-lamellar and nano-SiO_2 is copolymerized with MAA monomers completely. X-ray diffraction (XRD) results suggested that Na-MMT layers are exfoliated during the polymerization process.

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