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Preparation and Application of a Nanocomposite (MPNS/SMA) in Leather Making

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Abstract: A nanocomposite of MPNS/(Styrene-maleic anhydride) was prepared by the polymerization of methacryloxypropyl nano SiO_2 (MPNS), styrene (ST) and maleic anhydride (MA) with benzoyl peroxide (BPO) as initiator in toluene. The prepared samples were characterized by Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscope (TEM). Meanwhile, the nanocomposite was applied as a tanning agent in leather making and the results showed that leather treated with MPNS/SMA nanocomposite has excellent quality.

Keywords: Nano-sized SiO_2, composite, polymerization, tanning agent.

Environmental pollution is one of headache problems in leather tanning industry. Traditionally chrome tanning was the predominant technique used in leather making. However, chrome tanning is being substituted due to its pollution and scarcity of resource. The study of non-chrome tanning in leather shows more interests with the development of nanomaterial and nanotechnology. J. Z. Ma *et al.* have reported that organic–montmorillonite nanocomposite can raise the shrinkage temperature of pickled pigskins by 17 ºC [1].

It is known that nano SiO_2 is an environmentally friendly inorganic nonmetal material. The performance of resinic materials will be improved comprehensively, when nano-sized SiO_2 are dispersed equably and adequately into them. For example, the transparence, intensity, tenacity and aging resistance of polystyrene plastic film are enhanced with nano-sized SiO_2. These specialities show that polymers comprised with nano SiO_2 have an immense application potential in leather making process[2,3]. In this paper, we reported the synthesis of the new nanocomposite (MPNS/SMA) and explored its application in tannage of sheepskins. MPNS/SMA showed better tanning effects than traditional chrome tanning, which can be expected to have commercial value in current leather industry.

Methacryloxypropyl nano SiO_2 (MPNS) was obtained from Nano Engineering and Technology Center of Henan Province. The double bond introduced onto the surface of

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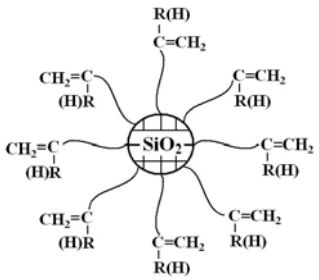
the nano-sized SiO_2 was determined by mercury salt bromination with catalytic method. The double bond content was 90 g I_2/100g. The particle size was 10 nm and the schematic view of its structure is shown as follows:



Styrene was washed with 5 % sodium hydroxide solution, dried over barium oxide and distilled twice under vacuum. Benzoyl peroxide (BPO) was recrystallized from chloroform. Toluene was distilled from sodium before use. All other chemicals were commercially available without further treatment. The synthesis of MPNS/SMA nanocomposite tanning agent was carried out as follows[4-6]: 2 g MPNS, 10.4 g ST and 9.8 g MA were dispersed ultrasonically in 100 mL dried toluene for 15 min. The mixture is transferred into a 250 mL four-neck flask, then heated to 55 ºC with stirring. A solution of 0.2 g BPO in 30 mL toluene was dropped tardily for 30 min. After that, the mixture was heated at 85 ºC for 3 h. After cooling, the precipitate was filtered and dried in vacuum at 40 ºC for 12 h. The dried product was neutralized with 5 % sodium hydroxide solution, then the final product was obtained as a pale yellow viscous liquid.

IR spectra was obtained on an Avatar 360 FT-IR. **Figure 1** shows the FT-IR spectra of MPNS (**Figure 1a**) and MPNS/SMA (**Figure 1b**). The bands, 1100 cm^{-1} of Si-O-Si, 1698 cm^{-1} of C=O and 1652 cm^{-1} of C=C group in the spectrum of MPNS. The bands, 1089 cm^{-1} of Si-O-Si, 831cm^{-1} of Si-O-C group, 1856 cm^{-1}, 1778 cm^{-1}, 703 cm^{-1} and 758 cm^{-1} were the evidence of success of polymerization of ST, MA and MPNS.

Figure 1 FT-IR of (a) MPNS and (b) MPNS/SMA

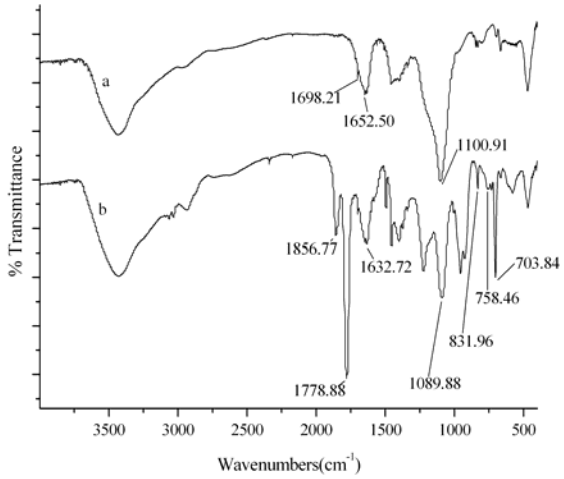
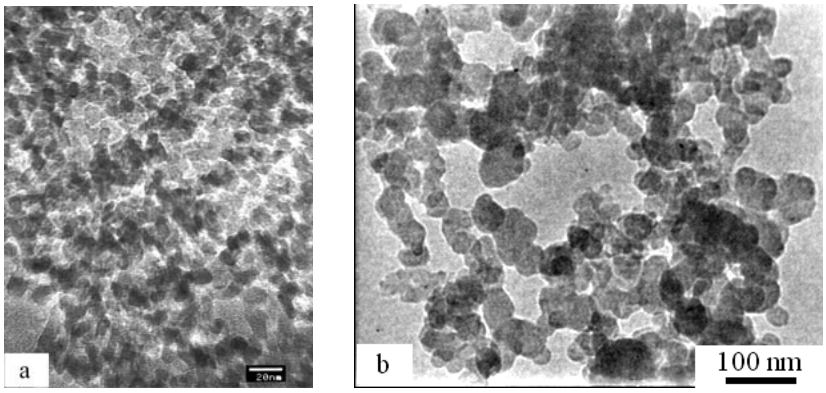


Figure 2 TEM images of (a) MPNS and (b) MPNS/SMA



TEM images were taken on a JEM-2010 high resolution transmission electron microscope. **Figure 2** shows the TEM images of MPNS (**Figure 2a**) and MPNS/SMA (**Figure 2b**). It was observed that MPNS/SMA has the larger grain size (30-70 nm) than MPNS (10 nm), which showed that the polymers were grafted successfully onto the surface of the nano-sized SiO_2 and improved its dispensability. MPNS/SMA has a particle size of 30-70 nm, which not only easily but also effectively penetrate into the leather. The better tanning and filling properties of MPNS/SMA may associate with its wider particle diameter distribution.

MPNS/SMA nanocomposite was used as a tanning agent on pickled sheepskins. The amount of tanning agent employed in the process was 4 % of total solid content based on pelt weight. The tanning process is described as follows:

8 % NaCl, 100 % water and the pelts were added into the drum, run for 20 min. Then 1 % formic acid (diluted 1:10 with water) was added to the pelts and run for 1 hr. The pH of the liquor in the drum was 4.0. Next portion 4 % MPNS/SMA was added. The running was then continued for 8 hrs. After that, sodium bicarbonate (diluted 1:20 with water) was added and run for a further 1 hr. The final liquor pH was 6.0.

As shown in **Table 1**, MPNS/SMA composite can raise the shrinkage temperature of pickled sheepskin by 20 ºC and increase thickness by 75.6 %, the results showed that MPNS/SMA has good tanning and filling properties[1,7]. It is probably due to the introduction of nano-sized SiO_2 into the molecules which can produce the netlike combination of the tanning agent with collagen and a form more hydrogen bonds between the tanning agent and collagen[8], simultaneously, the coordinate bonds can be formed.

Table 1 Results of tanning with MPNS/SMA

	Shrinkage temperature (ºC)	Thickness increment ration (%)
Before tanning	48	
After tanning	68	75.6
ΔTs	20	

Table 2 Physical mechanical tests of retanned leathers by MPNS/SMA and chromate powder

	Chromate powder	MPNS/SMA	Increment ratio (%)
Tensile strength (N/mm^2)	18.28	21.38	16.96
Tear strength (N/mm)	46.77	53.43	14.24
Break elongation ration (%)	60.83	72.95	19.92

Meanwhile, the paralleled experiments were carried out between MPNS/SMA composite and chrome tanning. The physical-mechanical properties of the leather were measured and compared, as shown in **Table 2**. It can be seen that the leather retanned with 1 % MPNS/SMA composite has the better strength and flexibility than that retanned with 1 % chromate powder based on weight of wet blue sheep leather. These results indicated that MPNS/SMA has a better retanning effect than chromate powder. Further studies are to be pursued.

Furthermore, the application test showed that the shrinkage temperature of the tanned leather by MPNS/SMA can reach more than 95 ºC with use of 2 % chromate powder on pickled pelt weight. The amount of chrome can be reduced significantly. The leather treated with MPNS/SMA has the better quality, such as fullness, fine grain and softness.

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