

PREPARATION OF ACRYLIC RESIN/MONTMORILLONITE NANOCOMPOSITE FOR LEATHER TANNING AGENT

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ABSTRACT

An acrylic resin/montmorillonite (AR/MMT) nanocomposite was prepared using Na⁺-montmorillonite (Na⁺-MMT) via in-situ polymerization of hydrophilic monomer in aqueous medium. The synthesis conditions, such as the contents of MMT and ammonium persulfate (APS), the molar ratio of different monomers and the dosage of sodium bisulfite on the application properties of nanocomposite were investigated in detail. The thickness increment ratio, the wet-heat resistance and the tensile, slit and burst strengths of leather tanned by AR/MMT were improved and elongations at break and given load were slightly reduced, in contrast to AR treatment; the wet-heat resistance and the physical mechanical properties of leather tanned by 6% AR/MMT associated with 2% chromate were lower than 8% chromate tanned. Also, AR/MMT facilitates the absorption of chromate. Compared with conventional chrome tanning, the dosage of chromate is reduced 75%. Scanning Electron Microscope (SEM) pictures of leather samples indicated that the collagen fibers of leather samples tanned by AR/MMT are well dispersed when compared to AR and pure chromate treatment. X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) confirmed AR/MMT is an exfoliated nanocomposite.

RESUMEN

La nanopreparación de resina acrílica/montmorillonita (AR/MMT) fue preparada in situ con Na⁺-montmorillonita (Na⁺-MMT) a través de la polimerización del monómero hidrófilo en medio acuoso. Las condiciones de la síntesis, tal como el contenido de MMT y persulfato de amonio (APS), la relación molar de los diferentes monómeros, y la dosis de bisulfato de sodio, sobre la aplicación de las propiedades de la nanopreparación fueron investigadas en detalle. La proporción del incremento de espesor, la resistencia al calor en húmedo y la resistencia a la tracción, tensión de corte y ruptura del cuero curtido con AR/MMT se han mejorado y elongaciones a la rotura y carga dada se redujeron ligeramente, en contraste con el tratamiento con AR; la resistencia al calor húmedo y las propiedades físico/mecánicas de los cueros curtidos con un 6% AR/MMT asociados con un 2% de cromato fueron inferiores a los curtidos con 8% de cromato. Además, AR/MMT facilita la absorción de cromato. Comparado con el curtido al cromo convencional, la dosis de cromato se reduce en un 75%. Fotos de muestras de piel obtenidas mediante un microscopio electrónico de barrido (SEM) indican que la fibra de colágeno de las muestras de piel curtida por AR/MMT estaba bien dispersa en comparación con las tratadas con AR y cromato puro. Difracción de Rayos X (XRD) y Microscopía Electrónica de Transmisión (TEM) confirmaron que AR/MMT es un nanoproducto exfoliado.

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INTRODUCTION

In recent years, there has been a growing interest in the development of polymer-clay nanocomposites, in which nanometer-thick layers of clay are dispersed in polymers.¹ Nanocomposites exhibit improved or even novel properties when compared to micro- and macro-composites.^{2,3} Strong interfacial interactions between the dispersed clay layers and the polymer matrix lead to enhanced mechanical, thermal and barrier properties of the virgin polymer.⁴ So far, polymers such as polyimide, epoxy resin, polystyrene, polypropylene, polyvinyl alcohol and polyurethane, etc. have been studied in clay-based nanocomposites.⁵⁻¹¹ Choi et al.¹² prepared PEO/MMT nanocomposites by a solvent casting method using chloroform as a co-solvent. WAXD analyses and TEM observations established the intercalated structure of these nanocomposites. Weimer et al.¹³ prepared polystyrene / MMT nanocomposites via in situ intercalative polymerization method using a silicate-anchored initiator.

Up to now, polymer-clay nanocomposite has been widely used in the plastic, rubber and fiber fields. However, there is little research about polymer-clay nanocomposite used as a leather tanning agent. In our previous papers,¹⁴⁻¹⁵ acrylic resin/MMT (AR/MMT) nanocomposite was prepared by polymer solution intercalative. Here we prepare AR/MMT nanocomposite via in situ polymerization. The influence of the synthetic conditions such as the contents of MMT and ammonium persulfate (APS), the molar ratio of different monomers and the dosage of sodium bisulfite on the application properties of nanocomposite are investigated.

EXPERIMENTAL

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 Tianjin Chemical Reagent Factory. Acraldehyde (AL) was provided by Ke-long Chemical Plant, Chengdu.

Preparation of AR/MMT nanocomposite

Na-MMT (variable) and deionized water (70g) 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 (variable) 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 (variable) and sodium bisulphate (variable) were introduced into the mixture and stirred for 30min in the cool water bath, then the aqueous solution of APS (variable) and isopropyl alcohol were fed into the flask. The reaction was kept at 50°C

for 3h. (The content of monomers was 25% based on the weight of water. The contents of Na-MMT and APS were calculated on the weight of monomers. The contents of MAA and AL were expressed as the molar ratio of MAA and AL. The molar number of sodium bisulphate was based on the molar number of AL.)

Application of AR/MMT nanocomposite

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% AR/MMT 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. 2% chromate was added into solutions for 2 hours. The weights of using materials were all calculated based on leather weight. Chrome content of tanning waste liquids was determined by acidity potassium permanganate method.

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°-10°, using a Cu-K α incident beam ($\lambda=0.1546\text{nm}$), 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 morphology of the nanocomposite was observed by H-600 Transmission Electron Microscopy (TEM). The dispersion situation of collagen fiber was observed by Scanning Electron Microscopy (SEM). The physical mechanical properties of tanned leather were determined with GFU 55 Functional Materials Examination Machine made by Company (extending speed 100mm/min, backhaul speeding 100mm/min).

RESULTS AND DISCUSSION

Effect of MMT contents

Table 1 shows the wet-heat resistance temperatures and thickness increment ratios of leather tanned with 6% nanocomposites obtained at different MMT contents and 2% chromate. The wet-heat resistance temperature refers to the shrinkage temperature of leather in a certain heating medium. It reflects the stability of leather in wet and heat conditions. When the wet-heat resistance temperature is high, the leather in wet and heat conditions is more stable. According to Table 1, the wet-heat resistance temperature of leather tanned with 6% nanocomposites associated with 2% chromate can be improved to 91°C. However, the wet-heat resistance temperature of leather only treated with 2% chromate is 75°C. The improvement of the wet-heat resistance temperature of leather mainly results from carboxyl and aldehyde groups of nanocomposites. The aldehyde group of nanocomposites and amino group of the collagen molecular chain can form a

covalent bond.¹⁶ Moreover, the carboxyl group in the nanocomposite is crosslinked with the amino and hydroxyl group of collagen by an electrovalent bond and hydrogen bond.¹⁷ After being added to chromate, chrome not only crosslinks with the carboxyl group of collagen, but also bonds with the carboxyl group of the nanocomposite.¹⁸ Therefore, an interpenetrating network structure is formed (seen as Fig.1) and the stability of the leather in wet and heat conditions is improved.

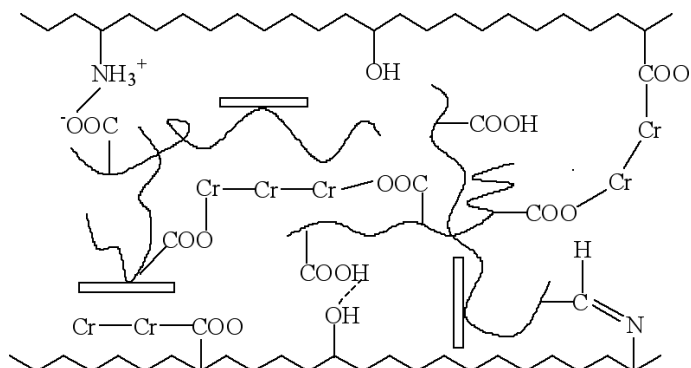


Figure 1. – The illustration of interpenetrating network structure.

The wet-heat resistance temperature of leather tanned with 8% chromate is about 98°C. This indicates used equal quantity nanocomposites instead of 6% chromate to treat with leather have the same effect as 8% chromate treat with leather. Hence, it can decrease the usage of chromate.

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 greater the thickness increment ratio, the fuller the leather is. The nanocomposites entering the collagen fiber are favorable for the increase in the thickness of the leather. As shown in Table 2, the thickness increment ratio of the leather tanned with nanocomposites associated with chromate is obviously higher than the leather only treated with chromate. When the dose of MMT is increased from 2% to 4%, the thickness increment ratio increases from 74.11 to 90.08. However, when the dose of MMT is increased further, the thickness increment ratio decreases.

Figure 2 provides the chrome contents change of waste liquids in which collagen was treated with nanocomposites at different MMT contents associated with chromate. The chrome content of waste liquids is increased along with an increase of the dose of MMT in nanocomposite. This mainly results from two reasons. One is reduction of polymer quality with the increase of MMT content. The other is the Lewis acid of the MMT crystal lattice edge deters free radical polymerization to some degree, and the silicate platelets hinder the polymer chain growth, leading to lower molecular weights.^{19,20} Therefore, the weight of polymer entered into

TABLE I
Properties of leather tanned with nanocomposites at different MMT contents

MMT/mt%	2	3	4	5	6
T ₁ /°C	45	46	45	46	46
T ₂ /°C	91	90	89	90	89
Thickness increment ratio/%	74.11	75.30	90.08	76.64	72.94

T₁: the wet-heat resistance temperature of leather;
T₂: the wet-heat resistance temperature of leather tanned with 6% nanocomposites at different MMT contents and 2% chromate.

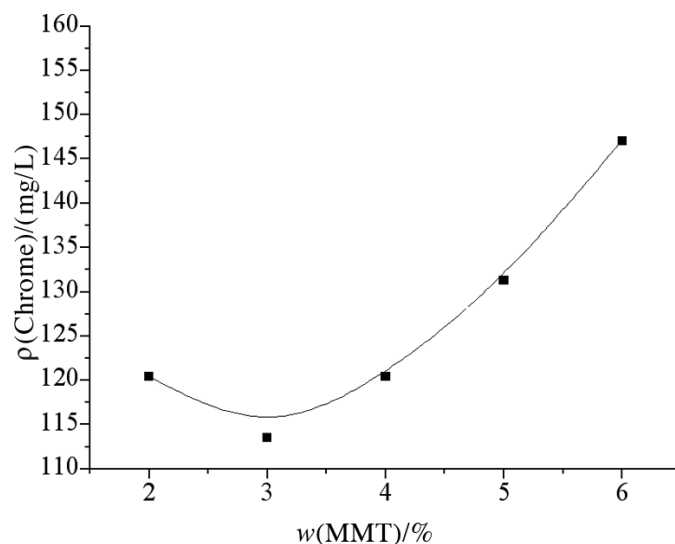


Figure 2. – Effects of AR/MMT nanocomposites with different MMT contents on ρ(chrome) of waste liquids.

collagen is less with the contents of MMT increasing. The combined point of chrome is less. Hence, the absorption ability of collagen to chrome is poor.

Effect of APS contents

Table 2 demonstrates that the influence of different APS contents on the application properties of the nanocomposite. The wet-heat resistance temperature and the thickness of leather after tanning were drastically improved. The wet-heat resistance temperatures of leather after tanning were almost kept invariable and the thickness increment ratio is decreased with the contents of APS increasing.

TABLE II

Properties of leather tanned with AR/MMT nanocomposites at different contents of APS

APS/mt%	6	7	8	9	10
$T_1/^\circ\text{C}$	36	35	36	37	36
$T_2/^\circ\text{C}$	91	93	91	91	92
Thickness increment ratio/%	100.01	79.55	74.11	71.89	69.31

T_1 : the wet-heat resistance temperature of leather;
 T_2 : the wet-heat resistance temperature of leather tanned with 6% nanocomposites at different contents of APS and 2% chromate.

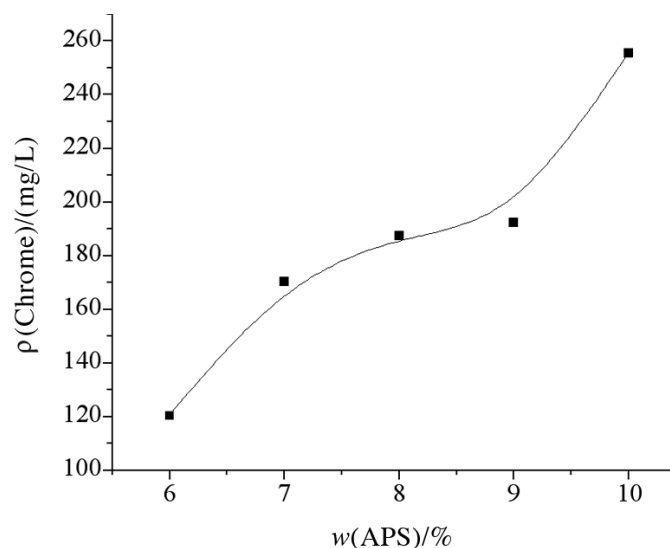


Figure 3. – Effects of AR/MMT nanocomposites at different contents of APS on $\rho(\text{chrome})$ of waste liquids.

Figure 3 shows that the chrome contents of waste liquids increase with the contents of APS increasing. The polymer of the high molecular weight is obtained with small APS content. Therefore, if the carboxyl group number of single molecule chain is higher, it facilitates the absorption of chrome.

Effect of the MAA/AL ratios

The influence of the different MAA/AL ratios on the application properties of the nanocomposite and the chrome content in waste liquids are shown respectively in Table 3

TABLE III

Properties of leather tanned with AR/MMT nanocomposites at different $n(\text{MAA}):n(\text{AL})$ ratios

$n(\text{MAA}):n(\text{AL})$	5:1	4:1	3:1	2:1	1:1
$T_1/^\circ\text{C}$	46	47	48	48	44
$T_2/^\circ\text{C}$	88	88	89	87	89
Thickness increment ratio/%	85.54	87.10	88.69	68.87	55.70

T_1 : the wet-heat resistance temperature of leather;
 T_2 : the wet-heat resistance temperature of leather tanned with 6% nanocomposites at different $n(\text{MAA}):n(\text{AL})$ and 2% chromate.

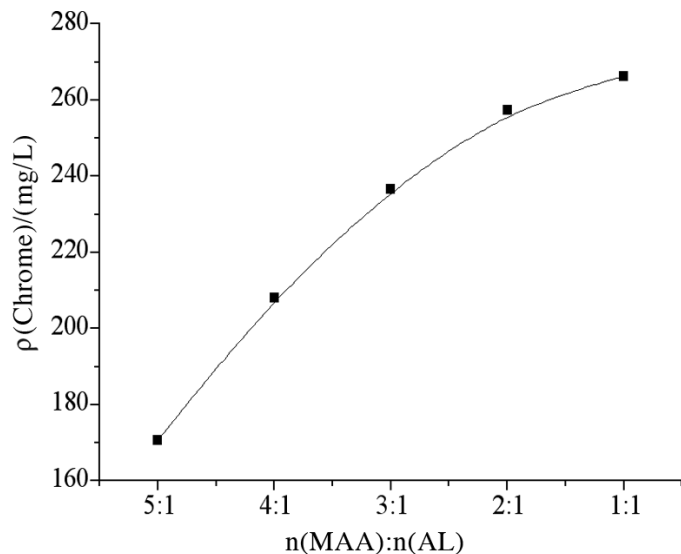


Figure 4. – Effects of AR/MMT nanocomposites at different $n(\text{MAA}):n(\text{AL})$ on $\rho(\text{chrome})$ of waste liquids.

and Fig.4. The incorporation of AL results in lightness increase and then decrease of the thickness increment ratio, but the difference of the wet-heat resistance temperature is slight. The chrome content in waste liquids was increased. The reason for this is that the number of carboxyl groups is reduced, when a greater amount of AL is used.

Effect of sodium bisulfite contents

Table 4 and Fig.5 represent the effect of sodium bisulfite contents on the application properties of the nanocomposite and the chrome contents in waste liquids, respectively. The

TABLE IV

Properties of leather tanned with AR/MMT nanocomposites at different n(NaHSO₃):n(AL) ratios

n(NaHSO ₃):n(AL)	1.0:1	1.2:1	1.4:1	1.6:1	1.8:1
T ₁ /°C	45	46	47	45	45
T ₂ /°C	92	90	89	91	88
Thickness increment ratio/%	110.14	114.47	96.38	104.13	93.31

T₁: the wet-heat resistance temperature of leather;
 T₂: the wet-heat resistance temperature of leather tanned with 6% nanocomposites at different n(NaHSO₃):n(AL) and 2% chromate.

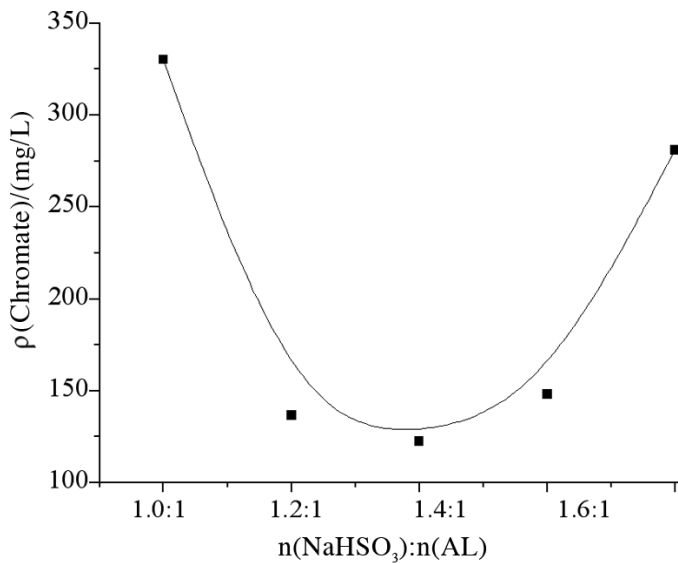


Figure 5. – Effects of AR/MMT nanocomposites at different n(NaHSO₃):n(AL) on ρ(chrome) of waste liquids.

best property of the nanocomposite is obtained with 1.2:1 of NaHSO₃/AL ratio used in the reaction. The main function of NaHSO₃ is the protective agent of aldehyde group and oxidation and reduction reaction system formed with APS. The introduction of NaHSO₃ can reduce the molecular weight of polymer. Therefore, there is appropriate molecular weight region that nanocomposite applied on leather tanning worked best.

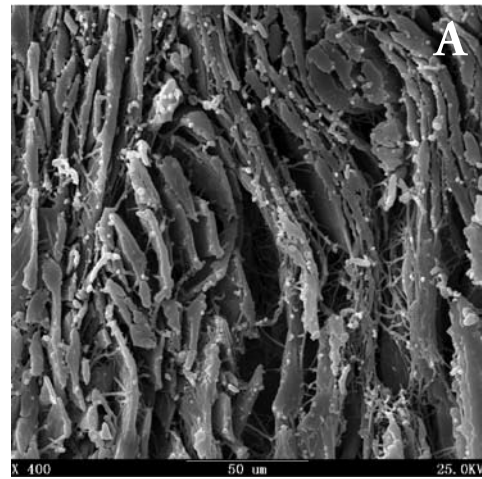


Figure 6a. – SEM picture of leather treated with AR/MMT nanocomposite and 2% chromate.

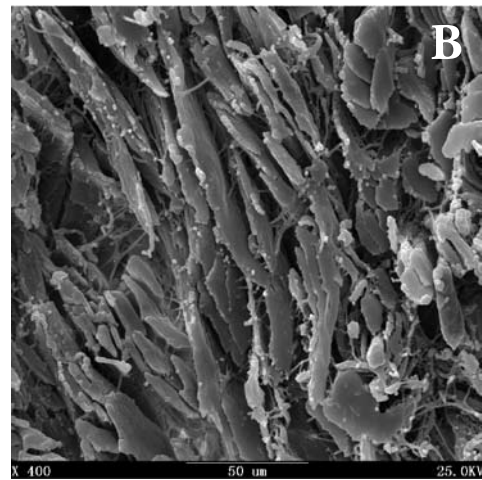


Figure 6b. – SEM picture of leather treated with pure polymer and 2% chromate.

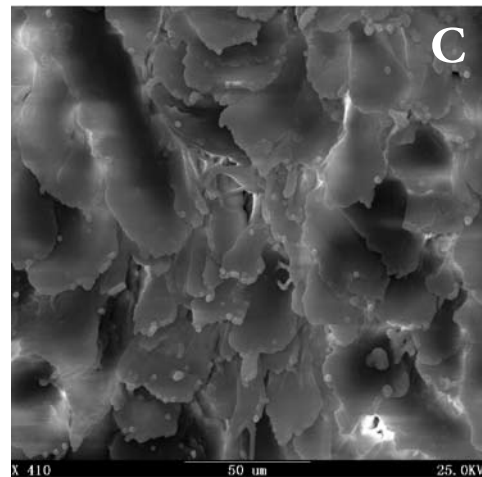


Figure 6c. – SEM picture of leather treated with 2% chromate.

Figs. 6a, 6b and 6c demonstrate collagenous fiber bundle is smaller and fibril is more in the SEM picture of leather treated with AR/MMT nanocomposite and 2% chromate than other pictures. AR/MMT nanocomposite has good dispersion property to collagen fiber.

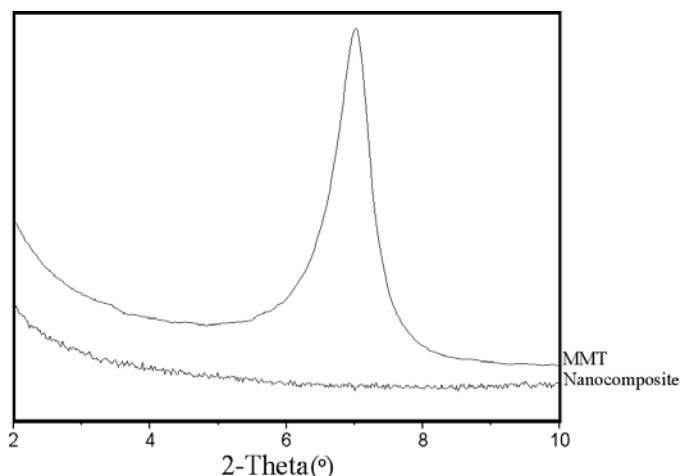


Figure 7. – XRD patterns of pristine MMT and nanocomposite.



Figure 8. – TEM image of nanocomposite.

The application properties contrast of AR/MMT nanocomposite, pure polymer and chromate

Table 5 demonstrates the thickness increment ratio, tensile strength, slit strength and burst strength of the leather tanned with AR/MMT nanocomposite associated with chromate increase in contrast to those of the leather tanned with pure polymer associated with chromate. However, the elongation at break and elongation at given load decrease. This is due to the introduction of MMT, which can increase rigidity and toughness, but decrease flexibility and plasticity. The wet-heat resistance temperature of the leather tanned with AR/MMT nanocomposite associated with chromate was approach to that of the leather tanned with 8% chromate. The thickness increment ratio was bigger and the physical mechanical properties were lower than those of the leather tanned with pure chromate.

The structure of AR/MMT nanocomposite

Fig.7 shows XRD patterns of pristine MMT and nanocomposite. A strong 001 characteristic diffraction peak of pristine MMT appeared at the 2θ value 7.02° , which corresponded to an interlayer d-spacing of 1.258 nm based on Bragg's equation. The nanocomposites did not show any noticeable XRD characteristic diffraction peak at the 2θ values from 2° to 10° . This result indicates that the clay platelets were probably exfoliated and dispersed in the polymer matrix. A TEM photograph of the nanocomposite is shown in Fig.8. The dark slices stand for the MMT layer. The polymer matrix appears as a light region. The MMT layers show good dispersion in the polymer matrix. Therefore, the nanocomposite formed is categorized as an exfoliated nanocomposite.

TABLE V

Tanning results of AR/MMT nanocomposite, pure polymer and chromate

	$\Delta T_s/^\circ\text{C}$	Thickness increment ratio/%	Tensile strength/ (N/mm ²)	Slit strength/ (N/mm)	Burst strength/ (N/mm)	Elongation at break /%	Elongation at given load /%
1	91	93.86	17.69	29.12	64.29	40.92	8.93
2	91	74.96	13.86	24.14	52.63	41.33	11.50
3	75	53.14	16.48	41.12	43.02	51.24	20.44
4	94	51.83	22.81	44.89	55.56	50.11	22.02

1.6% AR/MMT nanocomposite associated with 2% chromate treated collagen; 2. 6% pure polymer associated with 2% chromate treated collagen; 3. 2% Standard chromate treated collagen; 4. 8% Standard chromate treated collagen. (The dosage of materials is calculated based on 2 times collagen weight).

CONCLUSIONS

The application properties of the AR/MMT nanocomposite prepared via in-situ polymerization are strongly dependent upon the contents of MMT and ammonium persulfate (APS), the molar ratio of different monomers and the dosage of sodium bisulfite. The thickness increment ratio, the wet-heat resistance and the tensile, slit and burst strengths of leather tanned by AR/MMT were improved and elongations at break and given load were slightly reduced, in contrast to AR treatment; the wet-heat resistance and the physical mechanical properties of leather tanned by 6% AR/MMT associated with 2% chromate were lower than 8% chromate tanned. As well, AR/MMT facilitates the absorption of chromate. Compared with conventional chrome tanning, the dosage of chromate is reduced 75%. Scanning Electron Microscope (SEM) pictures of leather samples indicated that the collagen fiber of leather samples tanned by AR/MMT was well dispersed when compared to AR and pure chromate treatment. X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) confirmed AR/MMT is an exfoliated nanocomposite.

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