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# Characterization and Properties of Polymer Diallyldimethylammonium Chloride/Montmorillonite Nanocomposite Tannage

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**Abstract:** Polymer diallyldimethylammonium chloride (PDM) was prepared by free radical cyclopolymerization via ammonium persulfate and sodium thiosulfate as initiator. Polymer diallyldimethylammonium chloride/montmorillonite nanocomposite tannage (PDM/MMT) was prepared using two-steps method: montmorillonite (MMT) was modified with diallyldimethylammonium chloride (DM) through cation exchange reaction, and then cyclopolymerization of DM was carried out by free radical initiation in presence of MMT. The structure of DM, PDM and DM in nanocomposite PDM/MMT determined by Fourier Transform Infrared Spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) respectively. Nanocomposite tannage was applied in leather process and physics mechanical of performance of the resultant leather was measured. The results indicated that free radical polymerization of diallyldimethylammonium chloride could happen when montmorillonite exist in reaction system. Five ring of polymer was formed and did not effect by montmorillonite. XRD results indicated that the interlaminar distance of MMT in nanomaterial was reached biggest when the dosage of MMT was 5%, consistent with monomer translate ratio and characteristic viscosity of the polymer. Application results showed that nanocomposites tannage with 2% chromate tanned leather would increase leather shrinkage temperature increment ratio, incassation ratio, tensile strength and tear strength, compared with 2% chromate tanned leather.

**Keywords:** tannage; montmorillonite; cyclopolymerization; ammonium salt

## 1 Introduction

Tanning process is the most important process in the leather making. Chrome powder is a chemical used in the tanning process of the leather, which converts animal fibrous tissues of the natural leather to mineral fibrous tissue by adding tanning agents in the process. But with the excellence performance of leather, the chrome tan brings up serious environment problem. In recent years, environment problems have gotten more attention by people. The chromate used in leather making industry was considered as a poisonous chemical to environment. But due to its excellent tanning effects, it's not possible to substitute for it thoroughly at present. Leather industry is a traditional industry, but it also should absorb the advanced science and technology achievement.

Organic/inorganic nanocomposites have been extensively studied in recent years <sup>[1-3]</sup>. Especially in polymer/montmorillonite, it has become an importance part in organic/inorganic nanocomposites. By virtue of the layered montmorillonite (MMT), these nanocomposites show many desirable properties, such as improved modulus and strength, higher heat distortion temperature, enhanced barrier characteristics and reduced gas permeability. Jianzhong Ma prepared Vinyl Polymer/MMT <sup>[4]</sup> and polymer diallyldimethyl ammonium chloride /MMT <sup>[5]</sup> was applied in leather making process to examine its tanning properties.

In 1951, Butler reported that diallyl quaternary ammonium salts polymerized in the presence of catalytic quantities of tert-butylhydroperoxide to form water-soluble, noncrosslinked polymers <sup>[6]</sup>. A characteristic feature of the free-radical polymerization of allyl monomers is a cyclic intra and

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intermolecular polymerization mechanism<sup>[7]</sup>.

Polymers derived from radical cyclopolymerizations of 1, 6-dienes have two possible repeating cyclic structures, five- and six-membered rings. A six-membered ring and its radical formed during the propagation could be more stable than a five-membered ring and its radical formed, respectively. However, a five-membered ring is found quite often as a repeating unit in the polymers derived from 1, 6-dienes<sup>[8-9]</sup>.

For high positive charge, good water-solubility, controlled molecular weight, innocuity, inexpensive and so on, diallyl quaternary ammonium salts and its copolymerization has become an important part of water-solubility polymer. There are many reports about its research<sup>[10-14]</sup>.

For cation monomer, diallyldimethyl ammonium chloride could inter into inserted into the galleries of pristine MMT during ion exchange reaction. On the other hand, the monomer is a 1, 6-dienes compound, would occur in free radical polymerization and form five-membered ring or six-membered ring polymer. As an intercalating agent and reaction agent, diallyldimethyl ammonium chloride is a good monomer for preparing nanocomposite tannage by using in situ intercalation polymerization.

Should montmorillonite effect the polymerization of diallyldimethyl ammonium chloride when it endows many nano- properties with nanocomposite tannage?

In this paper, we prepared polymer diallyldimethyl ammonium chloride in exist of and without montmorillonite. For polymer in nanocomposites, influence of montmorillonite for polymer was discussed. PDM/MMT was applied in leather making process to examine its tanning properties.

## **2 Experimental**

### **2.1 Reagents**

Diallyldimethyl ammonium chloride was purchased from the Huangshan chemical Reagent Co. in Haining (China) without further purification. Pristine Sodium montmorillonite (Na-MMT) with a cation exchange capacity (CEC) of 89.38 mequiv/100 g was obtained from Qinghe Chemical Plant, China. The ammonium persulfate and sodium thiosulfate used were of analytical grade, which were purchased from Yuming Chemical Reagent Plant in Tianjing (China) and Xi'an Chemical Reagent Plant (China) respectively.

### **2.2 Preparation and methods**

#### **2.2.1 Preparation of poly diallyldimethyl ammonium chloride**

A 250ml 3-necked round-bottom flask equipped with a magnetic stirrer, reflux, and addition funnel. The reactor flask, charged with 60wt% diallyldimethyl ammonium chloride based on H<sub>2</sub>O, were immersed in a water bath at 60°C. During this time, ammonium persulfate and sodium thiosulfate as initiator were added by using funnel in 15min respectively. The mixture was stirred and heated at 60°C for 5h. The crude polymer diallyldimethyl ammonium chloride was obtained. The production was washed with acetone and absolute alcohol, filtrated until it became to white solid. The white polymer was dried under a vacuum at 65°C until it reached a constant weight.

#### **2.2.2 Preparation of poly diallyldimethyl ammonium chloride/ montmorillonite nanocomposite (PDM/MMT)**

The reaction was carried out in a three-necked round-bottom flask equipped with stirred, condenser and addition funnel. 60wt% diallyldimethyl ammonium chloride based on H<sub>2</sub>O was added in flask. Stirred slowly, some montmorillonite based on diallyldimethyl ammonium chloride was dispersed in mixture system. The temperature was raised to 80°C, and the system was stirred vigorously by a blender for 4 hours. The mixture was then treated with ultrasound for 20 min. The mixture was stirred and

heated at 60°C, initiator were added by using funnel in 15min respectively. The system was stirred for 5h at 60°C. Polymer diallyldimethyl ammonium chloride/ montmorillonite nanocomposite was prepared.

### 2.3 Characterization and Measurement

XRD patterns of VP/O-MMT nanocomposites were obtained by using a Japan D/Max2200PC X-ray generator equipped with a Monochromator-filtered CuK $\alpha$  source. The diffractograms were scanned at the rate of 2°/min from 2 to 10°. All samples were dried in a vacuum oven for at least 24 h before XRD measurements.

NMR spectra were recorded using Mercury-200MHZ (Varian) or ARX-400 MHZ (BRUKE R) spectrometers. Samples were used for  $^1\text{H}$  spectrums and  $^{13}\text{C}$  spectrums in D $_2\text{O}$  respectively.

Fourier transform infrared (FTIR) analysis was performed using a FTS-65A Fourier transform infrared spectrometer. Spectra were obtained from powders.

### 2.4 Application of PDM/ MMT

PDM/MMT nanocomposite tannage was used as tanning agent in leather. The PDM/MMT nanocomposite tannage with 2% chrome was carried out on pickled sheepskins and is described in table 1.

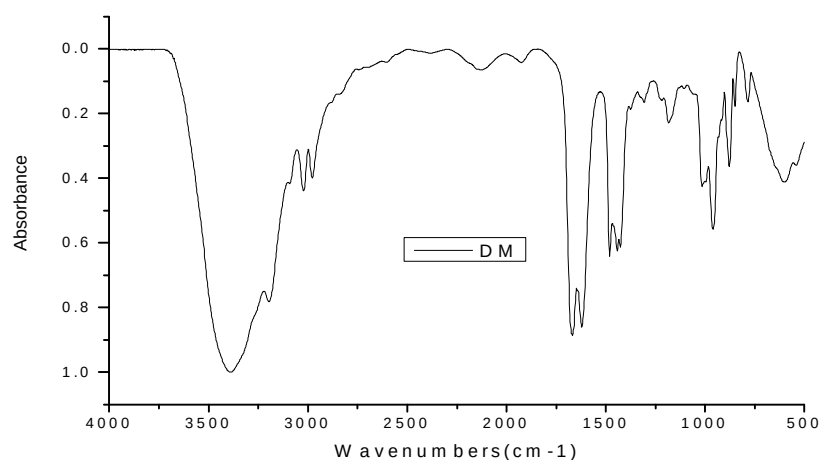
**Tab. 1 Chrome decreased tanning procedure**

| Operation                    | Products          | T(°C)             | Quantity (%) | Time     | Control                      |
|------------------------------|-------------------|-------------------|--------------|----------|------------------------------|
| Add to the drums             | NaCl              | R.T.<br>(ambient) | 8            |          |                              |
|                              | water             |                   | 100          | 15min    |                              |
| Put the pelts into the drums | Formic acid       | R.T.              | 0.2          | 30min    | Check pH=3.5                 |
|                              | PDM/MMT           |                   | 6            | 6h       |                              |
|                              | NaHCO $_3$ (1:20) |                   | 2            | 15min    | Check pH=4.0                 |
|                              |                   |                   |              | X3+20min |                              |
| Drain                        |                   |                   |              |          |                              |
| Washing                      | water             | R.T.              | 400          | 10min    |                              |
| Drain                        |                   |                   |              |          |                              |
| Chrome tanning               | water             | R.T.              | 80           |          |                              |
|                              | Chrome            |                   | 2            | 4h       |                              |
| Overnight                    |                   |                   |              |          |                              |
| Washing                      | water             |                   | 200          | 10min×2  |                              |
| Drain                        |                   |                   |              |          |                              |
| Fatliquoring                 | water             | 40                | 150          |          | The fatliquoring agents were |
|                              | SE                |                   | 4            |          | emulsified by hot            |
|                              | Sulfite fish oil  |                   | 2            | 2h       | water 60°C                   |
|                              |                   |                   |              |          | Check pH=3.8                 |
|                              | HCOOH(1:10)       |                   |              |          |                              |
| Washing                      |                   |                   | 1.5          | 30min×2  |                              |

## 3 Results and discussion

### 3.1 Diallyldimethyl ammonium chloride

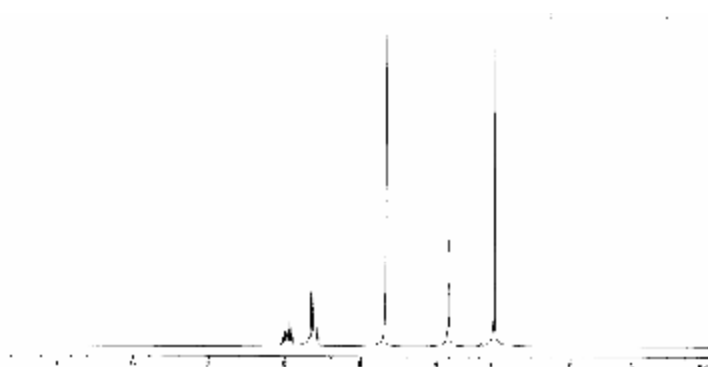
#### 3.1.1 Infrared



**Fig. 1 FT-IR of DM**

FTIR spectra of DM is shown in Fig.1. Since DM absorb water seriously, it is difficult to obtain the absolute dried sample, the peak at  $3450\text{cm}^{-1}$ ,  $2100\text{cm}^{-1}$  and  $1640\text{cm}^{-1}$  correspond to the water. The peak at  $3107\text{cm}^{-1}$  arises from C-H stretching vibration of  $=\text{CH}_2$ . The strong peak at  $1620\text{cm}^{-1}$  corresponds to stretching vibration of  $\text{C}=\text{C}$ . The peak at  $1015\text{cm}^{-1}$  causes from C-N stretching vibration.

#### 3.1.2 NMR spectroscopy



**Fig. 2  $^1\text{H}$ -NMR Spectra of DM**

The  $^1\text{H}$ -NMR spectra of the DM monomer is shown in Figure 2. Methyl protons give a single resonance peak at 2.930 ppm; the doublet peaks at 3.8210 ppm and 3.797 ppm are assigned to the methylene protons and are split ( $J = 7.4\text{ Hz}$ ) by the olefin proton ( $-\text{CHA}$ ). The triplet peaks at 5.575-5.866 ppm and 5.891-6.030 ppm are attributed to the olefin protons of the  $-\text{CHA}$  and  $\text{CH}_2\text{A}$ , respectively.

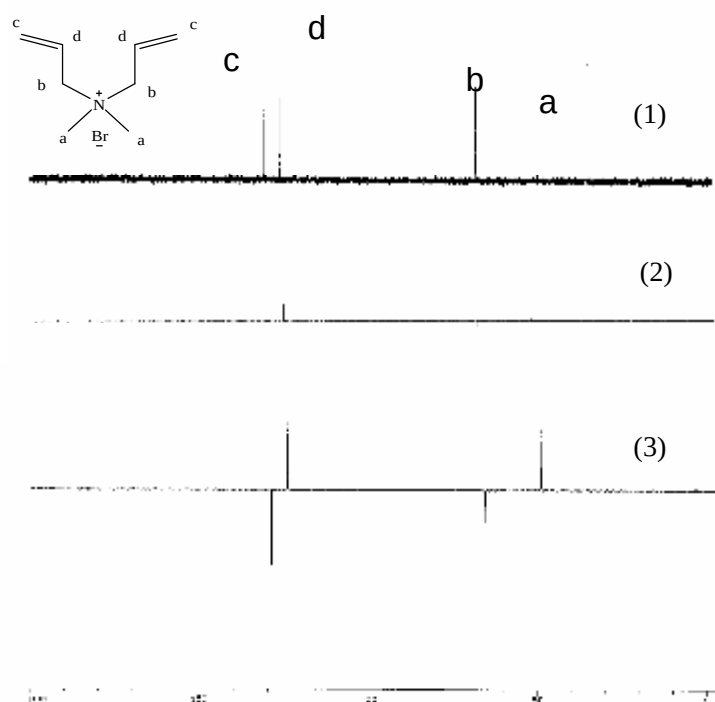


Fig. 3  $^{13}\text{C}$ -NMR spectra of (a) DM, (b) DEPT-90, and (c) DEPT-135

The  $^{13}\text{C}$ -NMR spectra of the DM monomer gave four peaks at 49.48ppm, 66.09ppm, 124.36ppm and 129.13ppm in Fig. 3(1) and the DEPT-90 [Fig. 3(2)] spectrum gave a single positive peak at 124.36ppm and are assigned to the carbon of methine ( $\text{ACH}-$ ). From the DEPT-135 [Fig. 3(3)] spectrum, the methylene carbons are observed as negative peaks at 49.48ppm and 124.36ppm while methyl and methine carbons are observed as positive peaks at 66.09 ppm and 129.13ppm.

### 3.2 Poly diallyldimethyl ammonium chloride

#### 3.2.1 Infrared

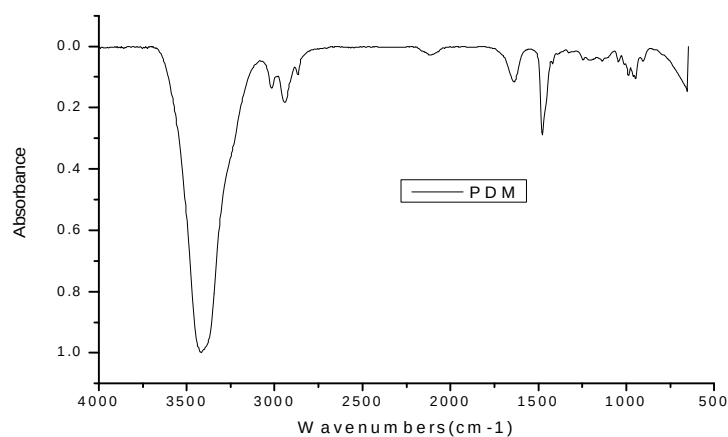


Fig. 4 FT-IR of PDM

An FTIR spectrum of PDM is shown in Fig.4. The peak at  $3107\text{cm}^{-1}$ ,  $1640\text{cm}^{-1}$  and  $877\text{cm}^{-1}\sim 990\text{cm}^{-1}$  almost disappeared, which indicates that the DM monomer was polymerized.

### 3.2.2 NMR spectroscopy

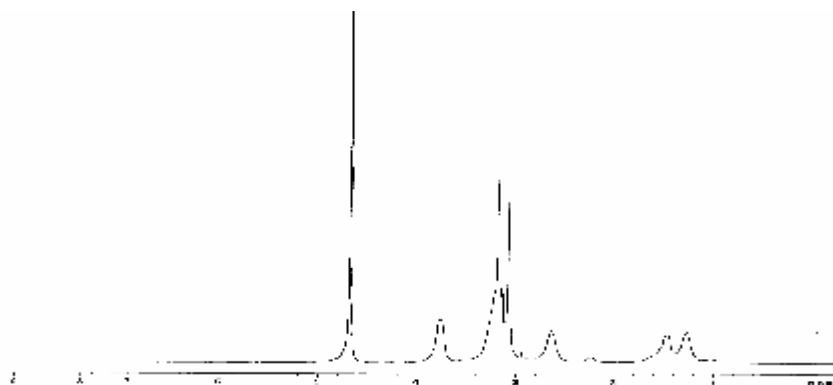


Fig. 5  $^1\text{H}$ NMR Spectra of PDM

From a comparison of Figure 2 and 5, it can be seen that the broad doublet peaks at about 1.4 ppm correspond to methylene protons and that methane gives a broad peak at about 2.642 ppm and that they are coupled each other. The multiplet resonance peaks at 3.1 and 3.760 ppm are assigned to methyl and methylene protons bonded with quaternary nitrogen.

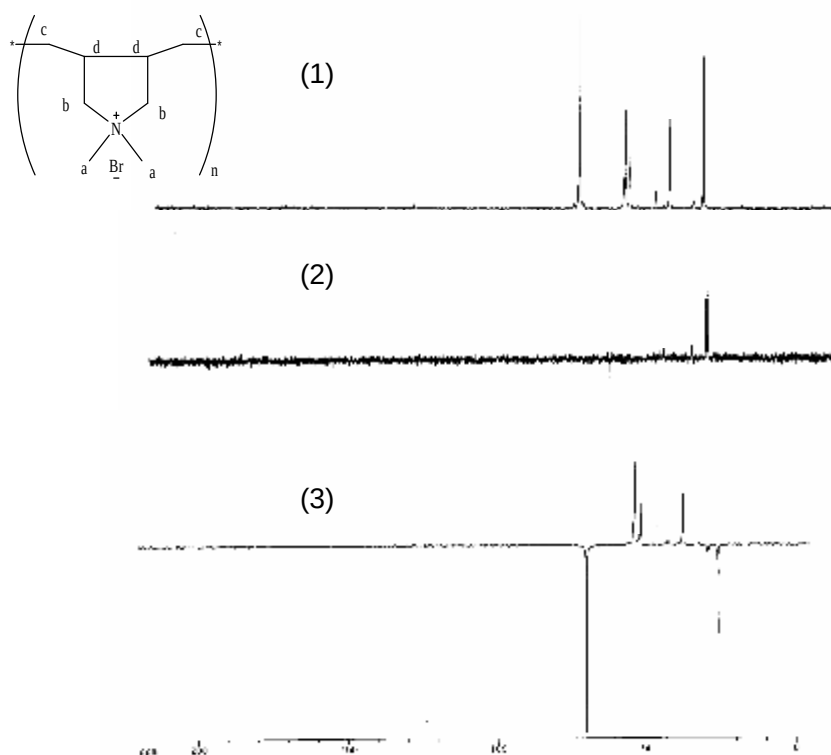


Fig. 6  $^{13}\text{C}$ -NMR spectra of (1) Poly (DM) and (2) DEPT-90 and (3) DEPT-135

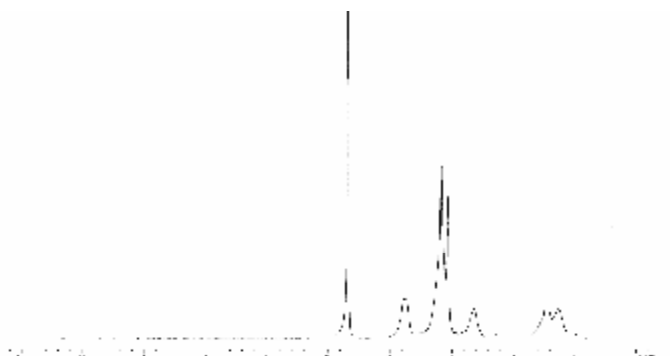
**Tab. 2 Carbon-13 Chemical Shifts of PDM (ppm)**

| Carbon                              | cis          | trans |
|-------------------------------------|--------------|-------|
| -CH-                                | 38.45, 38.04 | 43.20 |
| -CH <sub>2</sub> -CH <sub>2</sub> - | 26.27        | 29.98 |
| N <sup>+</sup> -CH <sub>2</sub> -   | 70.16        | 70.87 |
| N <sup>+</sup> -CH <sub>3</sub>     | 52.39, 53.87 | 54.57 |

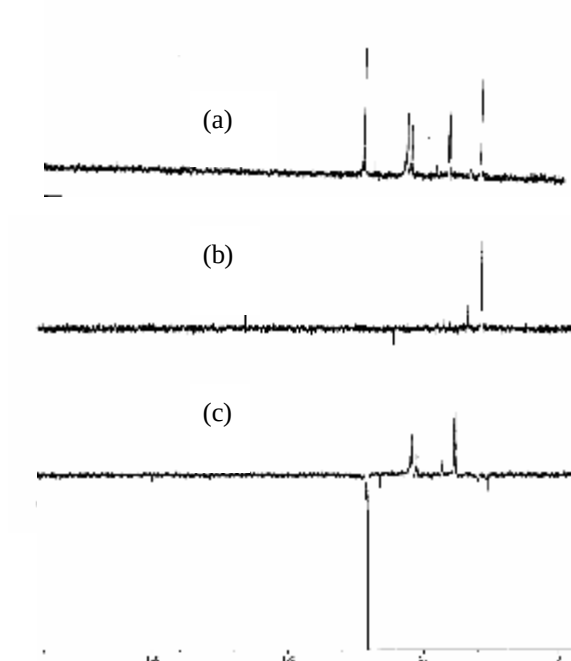
The <sup>13</sup>C spectrum of PDM is shown in Figure6, and the chemical shifts are summarized in Table2. The strong and weak peaks arise from the *cis* or *trans* isomers, with respect to the carbon–methyl substitutions. For the PDM compound, the N<sup>+</sup> methyls are nonequivalent in the *cis* isomer, but equivalent in the *trans* isomer. DEPT-135 [Fig. 6(3)] experiments were carried out to confirm the assignment.

### 3.3 Poly diallyldimethyl ammonium chloride from poly diallyldimethyl ammonium chloride/montmorillonite

#### 3.3.1 NMR spectroscopy



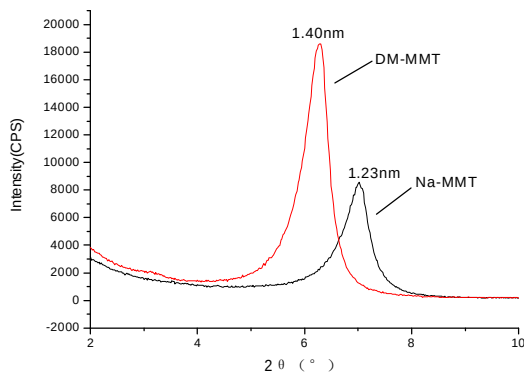
**Fig. 7 300<sup>1</sup>HNMR of PDM from nanocomposite**



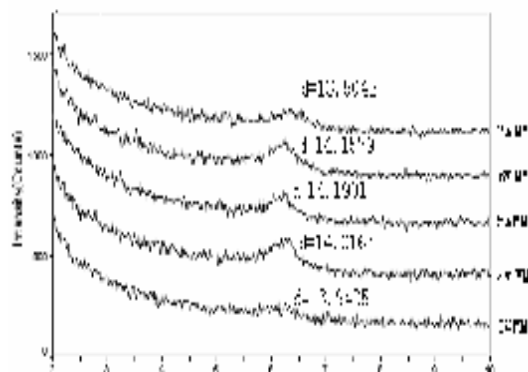
**Fig. 8  $^{13}\text{C}$ -NMR spectra of (a) PDM in nanocomposites and (b) DEPT-90 and (c) DEPT-135**

From a comparison of Figure 5, 6 and 7, 8, it can be seen that PDM from nanocomposite is still a five-ring structure, the structure of PDM is not influenced by montmorillonite.

### 3.4 Poly diallyldimethyl ammonium chloride/ montmorillonite XRD analysis



**Fig. 9 XRD spectra of Na-MMT and DM-MMT**



**Fig. 10 XRD pattern of PDM/MMT**

Fig.9 shows the XRD patterns of the pristine Na-MMT and DM modified MMT. The interlayer spacing of pristine MMT as received is 1.23nm. Evidently the  $d_{001}$ -spacing of the modified MMT is found to be increased up to 1.40 nm. This result confirms that the DM can be inserted into the galleries of pristine MMT.

Fig.10 is shown the  $d_{001}$ -spacing of nanocomposites, which prepared by different MMT dose. It is seen that increasing MMT dose from 3%-5% (of monomer weight) is accompanied by an increase of distance of the galleries of MMT. When the dose of MMT increases up to 5%, the distance of the galleries of MMT is decreases.

The ruler of characteristic viscosity of polymer in nanocomposites was consistent with XRD results<sup>[11]</sup>. The characteristic viscosity of polymer is bigger, the molecular weight is bigger. It indicated that polymer with big molecular weight could make the MMT's layer space bigger.

### 3.5 Application results of PVP / C-MMT

**Tab. 3 Shrinkage temperature increment ratio and thickness increment ratio of leather sample**

| Sample                        | 1     | 2     | 3     | 4     | 5     | 6     |
|-------------------------------|-------|-------|-------|-------|-------|-------|
| $\Delta T_s$ (°C)             | 31.5  | 33    | 30    | 28    | 27    | 29    |
| Thickness increment ratio (%) | 24.53 | 33.71 | 25.26 | 24.75 | 28.46 | 20.33 |

Note: 1- 5 PDM/MMT of content 3%、4%、5%、6%、7% MMT (based on 2 times of pelt weight) associated with 2% chromate tanned leather respectively;

6- standard 2% chromate (based on 2 times of pelt weight) tanned leather.

The data in table 3 show shrinkage temperature ratio and thickness increment ratio of leather sample. The shrinkage temperature ratio of sample 1-3 is all higher than sample 6. The thickness increment ratio demonstrates the extent of the thickness change before and after tanning. Generally, the bigger the thickness increment ratio, the fuller is the leather. The thickness increment ratio of sample 1-5



is larger than sample 6, indicating that the nanocomposite has a noticeable effect on the fullness of leather.

**Tab. 4 Mechanical properties of leather sample**

| Sample | tensile strength<br>P/(N/mm <sup>2</sup> ) | Increase ratio/% | Tear strength<br>p/(N/mm) | Increase ratio/% |
|--------|--------------------------------------------|------------------|---------------------------|------------------|
| 1      | 13.28                                      | 15.68            | 57.27                     | 2.87             |
| 2      | 13.32                                      | 16.03            | 61.11                     | 9.77             |
| 3      | 12.98                                      | 13.07            | 58.52                     | 5.12             |
| 4      | 13.25                                      | 15.42            | 55.32                     | -0.63            |
| 5      | 10.79                                      | -0.06            | 45.28                     | -18.66           |
| 6      | 11.48                                      | —                | 55.67                     | —                |

Note: same as table 3.

Seen from table 4, the tensile strength of sample 1-4 is bigger than sample 6. The tear strength of sample 1-3 is larger than sample 6. Whether is tensile strength or tear strength, sample 2 is increased to the largest. The results indicate that nanocomposite tannage could improve leather strength.

From the determinations above, it can be concluded that, the PDM/ MMT nanocomposite as tanning agent is a true low-chrome tanning agent with bright prospects.

#### 4 Conclusions

Poly dimethyldiallyl ammonium chloride (PDM) was prepared in our laboratory and monomer-to-polymer structures were characterized by proton, and carbon-13 nuclear magnetic resonance (NMR) as well as DEPT techniques. Poly diallyldimethyl ammonium chloride/ montmorillonite nanocomposite (PDM/MMT) was prepared by diallyldimethyl ammonium chloride occurred in free radical polymerization in exist of montmorillonite. Polymer in PDM/MMT also was characterized by proton, and carbon-13 nuclear magnetic resonance (NMR) as well as DEPT techniques. From the contrast results, it indicates that the structure of Poly dimethyldiallyl ammonium chloride is not influenced by montmorillonite exist. PDM/MMT was investigated by XRD. The results of XRD were in agreement with the monomer translate ratio and characteristic viscosity of polymer in nanocomposite. Preparation of poly diallyldimethyl ammonium chloride/montmorillonite nanocomposite in the condition of montmorillonite in existence, the molecular weight of PDM in PDM/MMT was influenced by dosage of MMT, but still kept the five-ring structure. Nano-composites were applied in leather making and physics mechanical of performance of the resultant leather was measured. Application results showed that nanocomposites would increase leather shrinkage temperature increment ratio, incrassation ratio, tensile strength and tear strength.

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