

# PREPARATION AND PROPERTIES OF POLY (VINYL CHLORIDE)/LAYERED SILICATE NANOCOMPOSITES

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## Abstract

A preparation of poly (vinyl chloride)(PVC) and dioctyl phthalate was mixed with 5 and 10 wt% of cloisite Na<sup>+</sup>, cloisite 30B or cloisite 93A. The obtained nanocomposites were characterized by thermal analysis using a thermogravimetric analyzer which shows that addition of 5 wt% of nanoclay to PVC increases its stability in the sequence: cloisite Na<sup>+</sup> < cloisite 93A < cloisite 30B. The electrical conductivity of these composites was studied as a function of temperatures and shows that the conductivity of PVC is enhanced using 5 wt% of nanoclay in the sequence: cloisite Na<sup>+</sup> < cloisite 30B < cloisite 93A. The activation energy for electrical conductivity is found to be lower for the composite containing 5 wt% of nanoclay in the same sequence. Increasing nanoclay content to 10 wt% shows some decrease in tensile strength, elongation %, and Young's modulus. X-ray diffraction and scanning electron microscopy were used for studying these nanocomposite structures and show better spatial dispersion of filler particles, when 5 wt% of cloisite 30B is introduced to PVC matrix.

## 1 Introduction

Filling polymers with particles has been largely used as a method to improve the mechanical properties of the resulting composite materials such as heat distortion temperature, hardness, toughness and mould shrinkage, as well as their fire resistance, electrical and thermal conductivity; especially at high filler content, sometimes more than 50 wt%<sup>1</sup>.

Polymer nanocomposites represent a new class of composite materials<sup>2,3</sup>, i.e. particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. Therefore, more interfacial interactions between the nanoparticles and between the nanoparticles and the

polymer matrix are expected which provide to the related composite materials improved properties at a much lower filler content; 3-5 wt%, comparable to those obtained for 30-50 wt% of micron-sized fillers<sup>4</sup>. Nanostructured polymers have received much attention in the field of material sciences because of their unique mechanical, optical, electrical and magnetic properties, and application in nano-materials and nanodevices. One of the main research and development domains is the fabrication of nanocomposites for the electronics industry where the rapid development of computers always demands smaller components. The most successful results have been obtained using layered silicates as nanofiller precursors, and more especially with montmorillonite<sup>5,6</sup> (MMT), a mica-type silicate which consists of sheets arranged in a layered structure. It is used due to its high achievable surface area (about 750 m<sup>2</sup>/g), platelet thickness of 1 nm, and high cation exchange capacity<sup>7</sup>. To improve the compatibility with polymer the intergallery cations (e.g. Na<sup>+</sup>) of the layered silicate can be exchanged with suitable alkyl ammonium salts as organic modifiers. By mechanical mixing with the polymer matrix this organically modified clay can be dispersed into small silicate stacks or even into single platelets with high aspect ratio. The resulting nanocomposites show large improvements in barrier properties<sup>8</sup>, flame resistance<sup>9</sup>, and dimensional stability, as well as in mechanical properties such as tensile strength, tensile modulus, and heat distortion temperature without a significant loss of optical transparency, toughness, or impact strength<sup>5,10</sup>.

The literature contains numerous studies about melt compounded nanocomposites using several polymer matrices such as nylon 6, epoxy resin, polystyrene, polypropylene, polyethylene, poly(ethylene oxide), polyimide, poly(methyl methacrylate), polyurethane and others<sup>11</sup>. Recently, poly(vinyl chloride)(PVC) nanocomposites started

receiving attention<sup>12,13</sup>. PVC is a polar polymer, therefore it is more convenient to use a polar modified type of clay. It is a rigid polymer, and hence dioctyl phthalate (DOP) is used as PVC plasticizer.

This paper aims at preparing three kinds of PVC/MMT nanocomposites. The next goal of this research work is to investigate the effect of adding 5 and 10 wt% of nanofiller particles on the mechanical properties (Young's modulus, tensile strength, and elongation %) as well as electrical properties (permittivity, dielectric loss, and electrical conductivity) of plasticized PVC. The study of the activation energy for electrical conductivity of PVC and its nanocomposites has been carried out. Morphology studies of PVC nanocomposites has been conducted using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

## 2 Experimental

### 2.1 Materials

In this work montmorillonite (MMT) obtained from Southern Clay Products, USA was used as nanofiller. Its silicate layers are approximately 200 nm long and 1 nm thick, and the interlayer spacing between stacked layers, denoted  $d_{001}$ , is about 1 nm<sup>14</sup>. Two different types of MMT were used: cloisite Na<sup>+</sup>, a natural MMT modified for higher Na content and two organophilic MMTs, cloisites 30B and 93A, which are types of Na<sup>+</sup> modified with two different quaternary ammonium salts. Cloisite 30B contains methyl tallow bis-2-hydroxyethyl ammonium cation at a loading of 90 meq/100g clay (Fig. 1), where tallow is ~ 65 % C<sub>18</sub>; ~ 30% C<sub>16</sub>; ~ 5% C<sub>14</sub>. Cloisite 93A contains methyl dehydrogenated tallow ammonium cation at a loading of 90 meq/100g clay (Fig. 2), where hydrogenated tallow is ~ 65 % C<sub>18</sub>; ~ 30% C<sub>16</sub>; ~ 5 % C<sub>14</sub>.

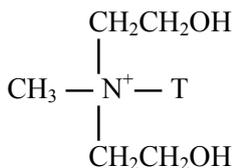


Fig.1. Chemical modifier of cloisite 30B

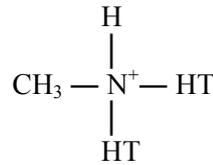


Fig.2. Chemical modifier of cloisite 93A

The suspension type of poly (vinyl chloride) (PVC) (K=67) was used as polymer matrix. Dioctyl phthalate (DOP) was used as PVC plasticizer and dibutyltindilaurate as a heat stabilizer.

### 2.2 Preparation of PVC/MMT Nanocomposites

A blend of poly(vinyl chloride) (PVC) and dioctyl phthalate (DOP) plasticizer was mechanically mixed with 5 and 10 wt% of cloisite Na<sup>+</sup>, cloisite 30B, or cloisite 93A and then compounded in Buss KO-kneader MKS 30 single screw extruder. Compounding was carried out at 130-160°C using a screw speed in the range of 25 to 45 rpm. Nanocomposites extrudates were thereafter palletized for calendaring.

### 2.3. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was conducted on a TGA7 thermal analysis system of Perkin Elmer Co. at a heating rate of 10 °C/min under a flowing air atmosphere. The temperature scan ranged from 30 to 600 °C.

### 2.4. Dielectric Measurements

The permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) for the prepared samples were measured at different frequencies ranging from 100 Hz to 100 KHz. An LCR meter (type AG-4311B) Ando electric LTD with the test cell NFM/5T was used. The capacitance C and the loss tangent ( $\tan \delta$ ) were obtained directly from the bridge from which  $\epsilon'$  and  $\epsilon''$  were calculated. The samples were in the form of discs of 58 mm diameter and 3 mm thickness. Calibration of the apparatus was carried out using standard samples (Trolitul, glass, and air) of 3 mm thickness; the accuracy for  $\epsilon'$  was  $\pm 1\%$  and for  $\epsilon''$  was  $\pm 2\%$ . The measurements were carried out at temperatures ranging from 30 to 100 °C using an ultrathermostat.

## 2.5. Electrical Conductivity Measurements

The electrical conductivity ( $\sigma$ ) of the investigated samples was measured by the application of Ohm's law using the NFM/5T test cell. A power supply unit (GM 45161/01) from Philips (the Netherlands) was used.

The potential difference  $V$  between the plates holding the samples and the current  $I$  flowing through it was measured by a multimeter (type URI 1050) from Rohde and Schwarz (Germany). The electrical conductivity is calculated using the equation:

$$\sigma = dI/AV \text{ mho } m^{-1} \quad (1)$$

Where  $d$  is the thickness of the sample in meters and  $A$  is its surface area in square meters.

## 2.6. Mechanical Measurements

Tensile strength, elongation %, and Young's modulus were measured using an Instron testing machine (model 1026) at  $23 \pm 2^\circ\text{C}$  with a crosshead speed of 100 mm/min, a chart speed of 200 mm/min, and a load cell range of 0-500 Newton full scale according to ASTM D 638.77a<sup>15</sup>. The dimensions of the sample were 3 mm thickness, 4 mm width, and 20 mm length. The mean value of five measurements for each sample was taken. The results are given in Table 2.

## 2.7. X-ray diffraction Measurements

X-ray diffraction (XRD) patterns were obtained using Siemens D500 diffractometer with back monochromator and Cu anticathode (step  $0.02^\circ$ , step time 2s). Special attention was paid to the low  $2\theta$  region for accurate determination of  $d_{001}$ , i.e. the nanoclay  $d$ -spacing.

## 2.8. Scanning Electron Microscope Testing

Phase morphologies were studied using a JEOL JSM-T20 scanning electron microscope (SEM). For scanning electron observation the surface of the polymer was mounted on a standard specimen stub. A thin coating ( $\sim 10^{-6}$  m) of gold was deposited into the polymer surface and

attached to the stub prior to SEM examination in the microscope to enhance the conductivity and secondary electron emission characteristic of the overgrowth.

## 3 Results and Discussion

### 3.1 Thermogravimetric Analysis

The thermal stability of prepared composites has been studied using a thermogravimetric analyzer (TGA). Thermogravimetric behavior could be used as a proof of the interactions between the organic medium and inorganic nanoplatelets surface. The thermal stability of plasticized PVC and its composites using the TGA thermogram shows that they are stable with no weight loss up to  $100^\circ\text{C}$ . The degradation in plasticized PVC and its composites using cloisite  $\text{Na}^+$  (5 wt%), cloisite 93A (5 wt%), cloisite 30B (5 wt%), cloisite  $\text{Na}^+$  (10 wt%), cloisite 93A (10 wt%), and cloisite 30B (10 wt%) starts above  $100^\circ\text{C}$  and continues up to  $526.33$ ,  $531.02$ ,  $539.07$ ,  $548.48$ ,  $526.40$ ,  $528.97$ , and  $532.91^\circ\text{C}$ , respectively. At these temperatures, the percentages of degradation are 99.090, 97.969, 97.168, 96.524, 95.389, 94.678, and 94.183 %, respectively. These data show that the largest delay of weight loss in air is observed for the nanocomposites containing 5 wt% of clay due to the barrier effect arising from the dispersion of the clay platelets<sup>16</sup> and that at higher filler content (10 wt%), the thermal stabilization is less efficient, probably as a result of a less optimal platelets dispersion (sterical hindrance). Data also show that the temperature of degradation is shifted towards a higher value when organophilic MMT is used compared to the polar clay. Thus, it could be concluded that organophilic treatment improves the thermal stability of PVC/clay nanocomposite, due to better interactions between PVC matrix and clay in the sequence: cloisite  $\text{Na}^+$  < cloisite 93A < cloisite 30B. The less thermal stability found for the composite containing nanofiller 93A than for that containing nanofiller 30B arises from the fact that cloisite 93A contains a ternary ammonium salt which is less thermally stable than quaternary ammonium salt present in the interlayer space of cloisite 30B.

## Electrical Properties

### 3.2.1 Dielectrics

Although polymer nanocomposites were found to enhance the gas barrier, thermal stability, mechanical strength, fire retardant, and corrosion resistance; their dielectric properties have been ignored in the researches. Therefore, the present paper will focus on studying dielectric measurements of the PVC nanocomposites in order to modify selected properties for specific applications. The permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) for the prepared composites have been investigated in the frequency region from 100 Hz to 100 kHz at temperatures from 30 to 100°C. It is evident from Figure 3, which represents the variation of  $\epsilon'$  with frequency (f) at different temperatures for plasticized PVC and its composites containing 5 and 10 wt% of cloisite 93A, for an example, that the value of  $\epsilon'$  increases with increasing temperature and decreases with increasing frequency. Similar behavior was noticed before in the literature<sup>17-21</sup>. The increase of  $\epsilon'$  with temperature can be explained by the increase in the mobility of polar groups, a decrease in density, and hence, a decrease in the effect of the environment that facilitates the orientation of the mobile groups. The decrease of  $\epsilon'$  with frequency may be caused by dielectric dispersion. It is also apparent from Figure 4, which represents the variation of  $\epsilon''$  with frequency at different temperatures for plasticized PVC and its composites containing 5 and 10 wt% of cloisite 93A, that the value of  $\epsilon''$  is increased at higher temperatures, especially in the very low frequency region. The low frequency losses may be due to either the Maxwell-Wagner effect<sup>22</sup> as a result of an alternating current (ac) in phase with the applied potential or the direct current (dc) conductivity<sup>23,24</sup> resulting from the increase of ion mobility, or both. To confirm this, the dc conductivities of the investigated samples were measured by application of Ohm's law to the dc flowing through the samples at 200 V and at temperatures of 30-100°C. All samples showed appreciable dc conductivity. The dielectric losses caused by the dc conductivity ( $\sigma$ ) at the different frequencies ( $\omega$ ) are calculated using the equation<sup>25</sup>.

$$\epsilon''_{dc} = 9 \times 10^{11} \frac{4\pi \sigma}{\omega} \quad (2)$$

and subtracted from the values of  $\epsilon''$  in the low-frequency region. The data of  $\epsilon''$  after subtracting  $\epsilon''_{dc}$  are plotted against  $\log f$  and are represented in Figure 4. From this figure, it is clear that for all samples there is an absorption region at the different temperatures. As the temperature increases, the maximum loss peak increases and becomes clear.

It may be concluded that the low frequency losses are not totally dc losses and that they may comprise Maxwell-Wagner losses, because the differences between the permittivities and conductivities of the different ingredients in the investigated samples are relatively large.

### 3.2.2 Electrical conductivity

One of the interesting features of conductivity is its temperature dependence, which allows one to understand conduction mechanisms in materials. Figure 5 shows such a behavior in plasticized PVC and its composites containing cloisite Na<sup>+</sup>, cloisite 30B, or cloisite 93A. It is evident from this figure that the conductivity ( $\sigma$ ) of all composites increases with increasing the temperature from 30 to 100 °C due to the increase of the mobility of ionic bodies that takes place as a result of the excitation by heat. This characterizes semiconductor-like conduction in these composites. Furthermore, Figure 5 shows a pronounced increase in the value of  $\sigma$  of plasticized PVC at clay content of 5 wt%, especially at lower frequency region and higher temperatures in the sequence: cloisite Na<sup>+</sup> < cloisite 30B < cloisite 93A. The obtained values are between the two extremities of those of semiconductors ( $10^{-10}$  -  $10^{+2} \Omega^{-1} \text{cm}^{-1}$ )<sup>26</sup>. At 10 wt% content of the filler, the values of  $\sigma$  are clearly decreased. This may be attributed to the subsequent increase of the molecular weight of the PVC composite with further increase in the content of the filler which may have caused some steric hindrance that partially contributed to decreasing the mobility of the electric charges. In polymers, different conduction mechanisms are possible<sup>27,28</sup>. Almost all mechanisms are related to different types of polarization taking place in the system. Each of these mechanisms predominates in a given temperature range and applied electric field.

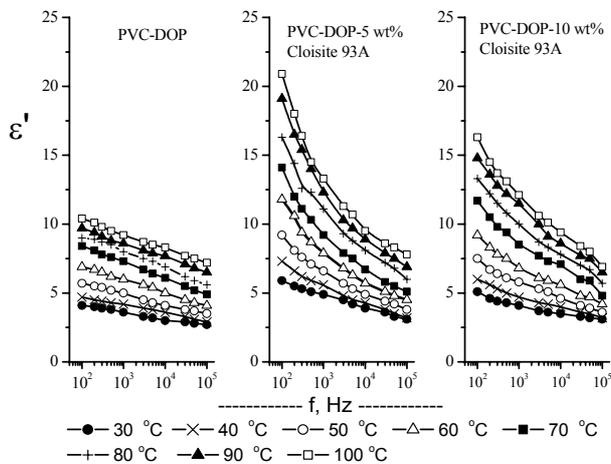


Fig. 3: The permittivity ( $\epsilon'$ ) versus frequency ( $f$ ) for PVC-DOP mixed with cloisite 93A

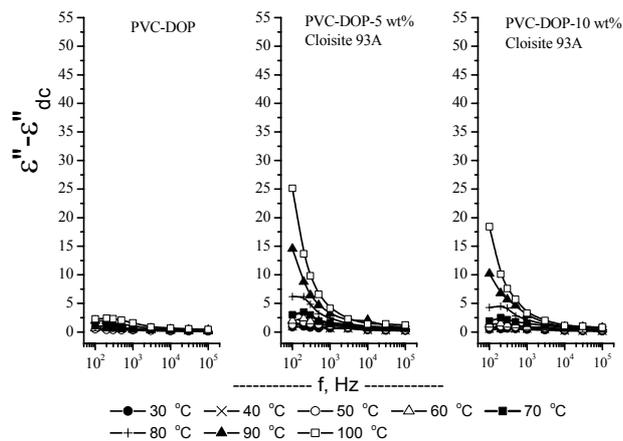
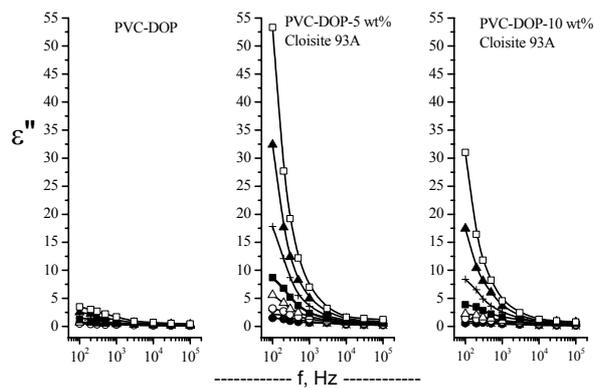


Fig. 4: The dielectric loss ( $\epsilon''$ ) and ( $\epsilon'' - \epsilon''_{dc}$ ) versus frequency ( $f$ ) for PVC-DOP mixed with cloisite 93A

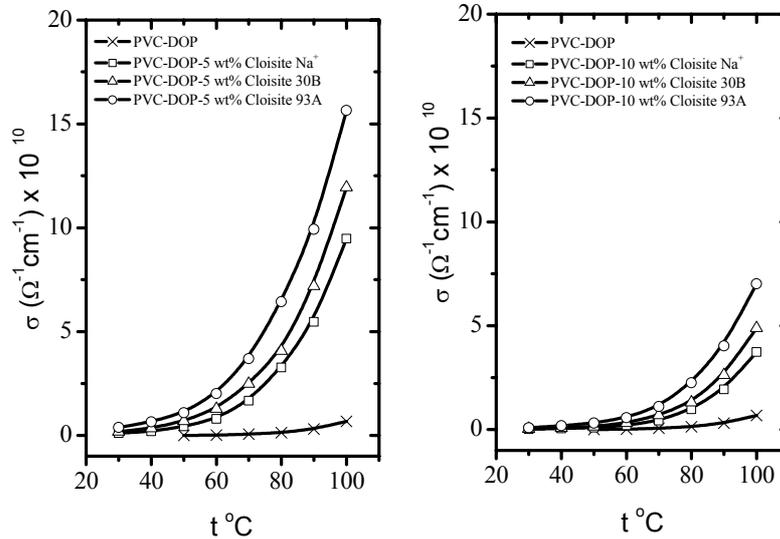


Fig. 5: The relation between electrical conductivity ( $\sigma$ ) and temperature ( $t$ ) for PVC-DOP mixed) with cloisite Na<sup>+</sup>, cloisite 30B, and cloisite 93A

### 3.2.3 Activation Energy for Electrical Conductivity

The activation energy ( $E$ ) for electrical conductivity ( $\sigma$ ) of plasticized PVC and its composites was calculated by plotting the logarithm of the conductivity against the reciprocal of the absolute temperature where a straight line was obtained, as shown in Figure 6, showing that the PVC composites of cloisite Na<sup>+</sup>, cloisite 30B, or cloisite 93A tend to behave as semiconductors. From the slope of the straight line,  $E$  was calculated using the equation<sup>29</sup>

$$\sigma = \sigma_0 e^{-E/RT} \quad (3)$$

It has been found that the period of excitation depends on the activation energy needed to make the substance conducting. If the activation

energy is low i.e. the system is easily excited the PVC composite becomes semiconducting at room temperature or in the presence of indirect light. Hence, it can be used for electronic devices working at normal temperatures. It is apparent from Table 1 that the activation energy for electrical conductivity of plasticized PVC decreases at the clay content of 5 wt% and decreases to a lesser extent at 10 wt% content of the filler in the sequence: cloisite Na<sup>+</sup> < cloisite 30B < cloisite 93A. The lowest value of the activation energy of PVC/5 wt% cloisite 93A nanocomposite (5.30 K cal/mol) indicates that it is easily excited and tends to behave as a semiconductor, and can be better employed for electronic and microwave nanodevices.

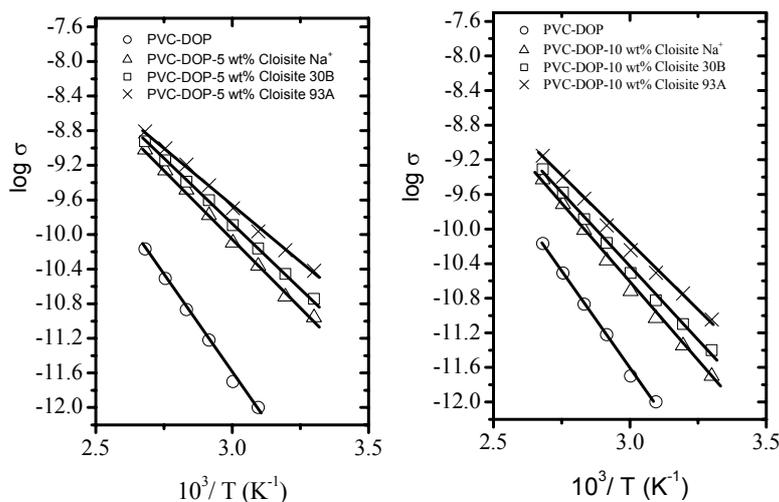


Fig. 6: The relation between  $\log \sigma$  and  $10^3/T$  for PVC-DOP mixed with cloisite  $\text{Na}^+$ , cloisite 30B, and cloisite 93A

Table 1 . Activation energy of PVC-DOP mixed with 5 and 10 wt% of cloisite  $\text{Na}^+$ , cloisite 30B, or cloisite 93A

Samples	Activation Energy (Kcal/mol)
PVC-DOP	9.13
PVC-DOP-5 wt% Cloisite Na	6.39
PVC-DOP-5 wt% Cloisite 30B	5.90
PVC-DOP-5 wt% Cloisite 93A	5.30
PVC-DOP-10 wt% Cloisite $\text{Na}^+$	7.65
PVC-DOP-10 wt% Cloisite 30B	7.21
PVC-DOP-10 wt% Cloisite 93A	6.45

### 3.2 Mechanical Properties

Mechanical properties tests (tensile strength, elongation %, and Young's modulus) were performed on PVC/ MMT nanocomposites with MMT loadings of 5 and 10 wt% , and the results are listed in Table 2 . The presented data show that the tensile strength , elongation % , and Young's modulus of the three PVC/MMT nanocomposites are increased significantly at 5 wt% of MMT loading in the sequence :cloisite  $\text{Na}^+$ < cloisite 93A < cloisite 30B. At 5 wt% content of nanofiller, the organic modifier increases the interaction between

the nanoparticles and PVC matrix, which leads to the breakdown of nanoparticle agglomerates, enhances nanoparticles dispersion in PVC, and improves interfacial adhesion between particle and matrix. Further increase of nanoparticles loading to 10 wt% in the composites brings about deterioration of tensile strength , elongation %, and Young's modulus in the sequence: cloisite  $\text{Na}^+$  < cloisite 93A < cloisite 30B ; but the composites still maintain good ductility. The decrease of the tensile strength may be caused by the poor interfacial adhesion between the PVC and filler phases as a result of the formation of some nanoparticle agglomerates at a higher degree of loading, leading to the retardation of crosslinks across the interfaces. The decrease of the elongation % may be due to an interstructural process in which the filler molecules are distributed in the interaggregate space.

It is significant to point out that TGA and mechanical measurements proved that organophilic clays are better candidates, compared to chemically untreated natural clay, to achieve a dispersion state leading to an improvement in the nanocomposites's final properties, such as thermal stability and mechanical behavior. This is because the nanoscale cloisite  $\text{Na}^+$  layers have high specific surface area and surface energy, which makes them tend to aggregate together rather than to disperse homogeneously in PVC matrix, especially at high MMT loadings.

Table 2 . Mechanical properties of PVC-DOP mixed with 5 and 10 wt% of cloisite Na<sup>+</sup>, cloisite 93A, or cloisite 30B

Samples	Tensile Strength (N/mm)	Elongation (%)	Young's Modulus (N/mm)
PVC-DOP	17.12	35.74	47.80
PVC-DOP-5 wt% Cloisite Na <sup>+</sup>	22.10	45.95	62.02
PVC-DOP-5 wt% Cloisite 93A	25.01	59.45	71.34
PVC-DOP-5 wt% Cloisite 30B	29.02	89.37	90.92
PVC-DOP-10 wt% Cloisite Na <sup>+</sup>	17.84	36.85	50.13
PVC-DOP-10 wt% Cloisite 93A	18.91	40.46	56.10
PVC-DOP-10 wt% Cloisite 30B	21.25	58.58	66.05

### 3.4 Morphology of PVC/MMT Nanocomposites

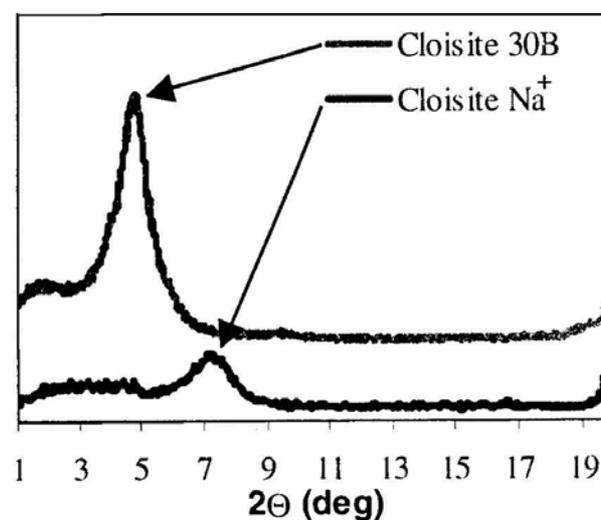
Nanostructures investigation has been conducted using X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements.

#### 3.4.1 XRD

X-ray diffraction is the most commonly used method for assessing the morphology of nanoclay in either powder form, or when compounded into a polymer matrix. The X-ray is reflected from each clay layer within a sample, therefore there is a relationship between the angle  $\theta$  and the physical spacing in the system. At the low angle values, the diffraction peak position is related to the extent of the interlayer spacing, according to the Bragg's law:  $\lambda = 2d \sin\theta$ , where  $\lambda$  is the wave length of the x-ray radiation used,  $d$  is the spacing between diffraction planes and  $\theta$  is the measured diffraction angle. The shift of diffraction peaks to the lower angle values shows an increase of the interlayer spacing. Therefore, the polymer matrix is most likely intercalated between clay layers forming a nanocomposite. For montmorillonite with poor interlayer spacing, the XRD pattern of the composite exhibits weak change of the basal diffraction peak intensity suggesting that nanocomposite structure is not achieved. One of the limitations is that X-ray diffraction analyses may

not always yield a unique interpretation of the data. Often, other techniques need to be used to complement the diffraction experiments<sup>30</sup>.

XRD characterization is generally based on the comparison between the diffraction peak position of the nanoclay powder and the nanoclay in the polymer matrix<sup>31</sup>. Figure 7 shows the maxima of cloisite 30B and cloisite Na<sup>+</sup>, for an example. The cloisite 30B shows a characteristic diffraction peak at 4.83° corresponding to basal spacing of 1.85 nm and the Na<sup>+</sup> MMT exhibits a single peak at 7.8°, corresponding to basal spacing of 1.2 nm.

Fig. 7. XRD pattern of cloisites 30B and Na<sup>+</sup>

In compounded samples (Figure 8) the expansion of the clay spacing by adding plasticizer and PVC between the platelets is evident. PVC/ 5 wt% cloisite Na<sup>+</sup> nanocomposite shows a characteristic diffraction peak corresponding to the (001) plane at 1.4 nm. This low interlayer spacing reveals that this nanocomposite has a low level of exfoliation of the clay in PVC matrix. The peak for the basal space of PVC/ 5 wt% cloisite 30B nanocomposite is not noticeable, a smoothly dropping diffractogram was obtained, therefore the nanofiller is fully exfoliated in PVC matrix.

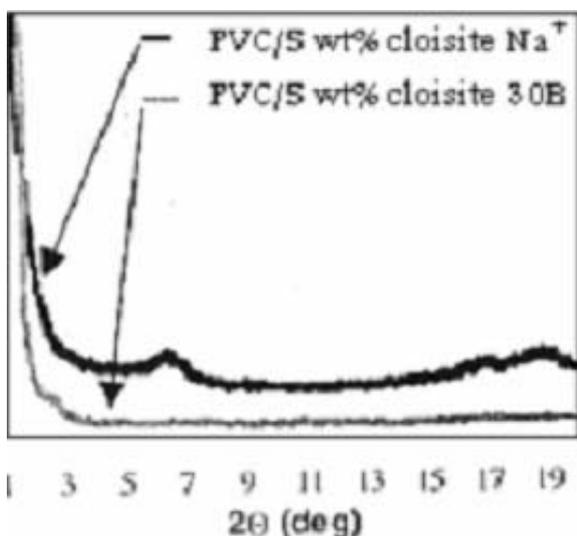


Fig.8. XRD pattern of PVC/cloisite 30B and PVC/cloisite Na<sup>+</sup> nanocomposites

### 3.4.2 SEM

Figure 9 shows SEM micrograph of pure PVC. Figure 10 also shows SEM micrograph of PVC/5 wt% cloisite 30B nanocomposite, for an example, and reveals that clay particles are dispersed homogeneously and no evidence of huge agglomerates is found. In opposite, when nanoclay content is 10 wt% the particles are very close surrounded by their "neighbours" and agglomerate formation occurred.

In conclusion, the interaction between PVC and MMT is an important factor influencing the morphology development of PVC/MMT nanocomposites.

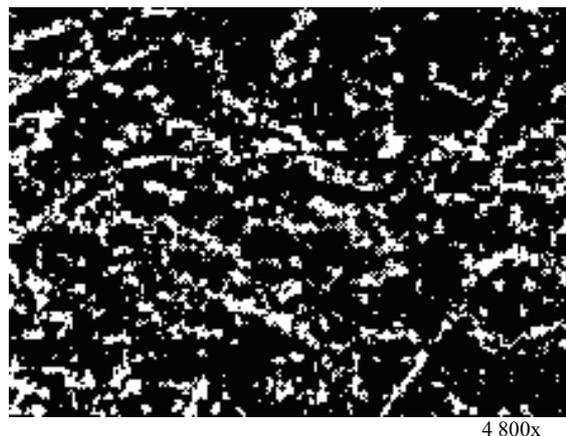


Fig.9.SEM micrograph of pure PVC



Fig. 10. SEM micrograph of PVC/5 wt% cloisite 30B nanocomposite -good exfoliation.

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