INFLUENCE OF CLAY ON MECHANICAL PROPERTIES OF POLYVINYL(ALCOHOL)/ MONTMORILLONITE MEMBRANES

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This work focused on the preparation of poly(vinyl alcohol) (PVA)/ silicate layers composites. Montmorillonite and
organically modified montmorillonite (MMT TEA and MMT HDTMA) were used for the PVA nanocomposites. The
membranes of poly(vinyl alcohol)/ modified montmorillonite composites were prepared by casting from a
polymer/silicate (3wt%) water suspension. The preparation of the materials was influenced by hydrogen bonds and the
hydrophobicity of the organophilic material. The obtained materials have different mechanical properties from the neat
PVA. In all cases, the mechanical properties were improved.

Keywords: membranes, polyvinyl alcohol, clay, montmorillonite, mechanical properties.

Introduction

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer employed in practical
applications because of its easy preparation, excellent chemical resistance and physical properties,
and because it is completely biodegradable. Recently, it has received much attention in non-fiber
applications specifically in pharmaceutical, biomedical and biochemical applications [1]. The poor
solvent resistance and antiageing properties, and insufficient mechanical properties have limited its
potential applications [2].

Recently, nanocomposites containing of PVA and layered materials are found to display novel
properties, which can be observed from two dissimilar chemical components combining at the
molecular level. There are several publications associated with the preparation and properties of
PVA–clay nanocomposite materials prepared by solution dispersion technique [3-5].

In 1963, Greenland [6] reported the first fabrication of PVA/MMT composites by a solvent casting
method using water as a co-solvent. After that Ogata et al. [7] used the same technique for the
production of PVA/MMT composites. Recently, Strawhecker and Manias [5] have also used solvent
casting method in attempts to produce PVA/MMT nanocomposites films. PVA/MMT
nanocomposite films were cast from a MMT/water suspension containing dissolved PVA.

In this work poly(vinyl alcohol) (PVA)/clay nanocomposites were prepared using the solution
intercalation method. Clay sodium montmorillonite (MMT), triethanol-ammonium chloride and
alkyl ammonium ion-exchanged clays (MMT_{HDTMA} and MMT_{TEA}) were used to prepare the PVA
composites. The membranes were characterized by X-ray diffraction (XRD) and tensile tests.

Results of Young modulus, tensile strength and elongation at break are presented and discussed.
Experimental

Materials
The polymer used was a commercial Poly(vinyl alcohol) (PVA), provided by ALDRICH (hydrolysis degree: 87-89%. M_w = 13000-23000). An Argentinean natural sodium montmorillonite (MMT) from Minarmco S.A. was used in this study.

Preparation of organophilic clay
The synthesis of the modified clays was realized in a reactor to disperse the MMT in water, with the addition of the corresponding salt: triethanolammonium chloride - TEA and hexadecyl trimethylammonium bromide - HDTMA in excess of 50% for one hour, at 80 °C. Clays obtained MMTTEA (exchanged with TEA) and MMTHDTMA (exchanged with HDTMA) were subjected to intensive washed and dried under reduced pressure at 60 °C.

Membrane preparation by casting
The composites were synthesized by a solution-intercalation film-casting method. The hybrid PVA films were cast from a MMT; MMTTEA; MMTHDTMA/water suspension. Distilled water was used to form a suspension of MMT (MMTTEA or MMTHDTMA) at room temperature. The suspension was stirred for 1 h and 30 min. The poly(vinyl alcohol) was added to the stirring suspensions such that the clay concentration was 3 wt %. The mixtures were then heated to 90 °C to dissolve the PVA, again stirred for 30 min, and finally films were cast at room temperature and controlled evaporated for 4 days. The film thickness was controlled from 0.14 to 0.22 mm by varying the total starting solution volume. PVA, PVA/MMT, PVA/MMTTEA and PVA/MMTHDTMA (3wt%) membranes were obtained.

Characterization
X-ray diffraction analyses (XRD) were performed in a Rigaku Miniflex DRX 600 diffractometer using nickel filtered CuKα radiation at 30 kV and 15 mA. The data were recorded at 20 rates of 2°/min.

The tensile tests were carried out using an Instron Universal Testing Machine, model 5569, at the crosshead rate of 10 mm/min, according to ASTM D882. All the specimens were conditioned at 50% RH and 23°C to the equilibrium. Were obtained tensile strength, Young’s modulus and elongation at break. At least five specimens were measured for each experimental condition and the average values were taken.
Results and discussions

In Fig.1, the powder XRD patterns show diffraction peak in $2\theta = 7.2^\circ$ for sodium montmorillonite, $2\theta = 6.5^\circ$ for the organophilics clays (MMT_{TEA}) and $2\theta = 4.7^\circ$ for MMT_{HDTMA}. The spacing of the MMT increased from 1.23 nm to 1.34 nm (MMT_{TEA}) and to 1.86 nm (MMT_{HDTMA}). It suggested the intercalation of hexadecyl trimethylammonium and triethanol ammonium in the interlayer space of MMT. In the preparation of organically modified montmorillonite, ionic interaction was expected between the positive charge of hexadecylamine (or triethanol-ammonium) and negative charge of the layer plane of MMT.

In Fig. 2, the powder XRD patterns show a diffraction peak in the PVA/MMT_{HDTMA} at $2\theta = 2.41^\circ$ (d spacing= 3.67 nm ), but for PVA/MMT and PVA/MMT_{TEA} the peak disappeared, indicating the possibility of having intercalated silicate layers of MMT_{HDTMA} and dispersed exfoliated pristine MMT and MMT_{TEA} in the PVA matrix.

The size of PVA molecules is large and it is very difficult for the entire PVA polymer chain penetrates between the layers. Nevertheless, the XRD diffraction patterns (Fig.2) indicated a high layer dispersion after the interaction of MMT, MMT_{HDTMA} and MMT_{TEA} with PVA. So, it seems that part of PVA chains or some small chains were intercalated into the inorganic layers.

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Figure 2. X-ray diffraction curves of: PVA, PVA/ MMT (3%), PVA/MMTTEA (3%) and MMTHDTMA (3%).

The tensile tests of PVA, PVA/MMT (3wt%), PVA/MMTTEA (3wt%) and PVA/MMTHDTMA (3wt%) composites are shown in Fig. 3. The Young’s modulus increased in all nanocomposites. The maximum enhancement of the stress at break (Fig.3) and Young modulus was observed for the PVA/MMT (3wt%) nanocomposite. Nevertheless, significant changes in the tensile stress at break and elongation at break were observed for these composite. The elongation at break decreases for PVA/MMTHDTMA composite (Fig.3).

The dramatic enhancement of the Young’s modulus for such extremely low MMT filler concentrations cannot be attributed simply to the introduction of the higher modulus inorganic filler layers. The observed effects can be attributed to regions of the polymer matrix that is bonded through different interaction forces (dipole-dipole, bond hydrogen) on the silicate surfaces, and is thus stiffened through its affinity and adhesion with the filler surfaces.
Figure 3. The Young’s modulus normalized by the bulk value (100 MPa), the break strength and break elongation of nanocomposites normalized by the bulk values (14.10MPa and 125.5%, respectively).

The chemical nature of PVA and clay layers surfaces can provide the interaction between the components probably of hydrogen and dipole-dipole bonding type. Such interactions can occur in pristine clay and modified clays, through the OH groups of polymer with Si-O-Si and OH groups of
clay, creating the process of exfoliation. A second expected interaction between $\text{MMT}_{\text{HDTMA}}$ and PVA is a non-polar interactions. As the HDTMA remained in the interlayer of $\text{MMT}_{\text{HDTMA}}$, the aliphatic hydrocarbon moieties of the HDTMA is placed into the interlayer of MMT, forming the hydrophobic spaces. So, as the PVA is partially hydrolyzed and the surface of the layers presented a certain level of hydrophobicity, the less polar ester groups of PVA could interact with the alkyl groups of the ammonium salt inside of the $\text{MMT}_{\text{HDTMA}}$ layers.

Conclusions

According to the XRD results, there is large level of interaction between molecules of PVA with the pristine clay (MMT) and modified clay with TEA (MMT$_{\text{TEA}}$). The membranes of PVA / MMT (3 wt%) and PVA / MMT$_{\text{TEA}}$ (3 wt%) show an exfoliated structure and that of PVA / MMT$_{\text{HDTMA}}$ (3 wt%) the coexistence of intercalated silicate layers and exfoliated seems to occur.

The chemical nature of polymer (PVA) and the surface the clay layers can provide hydrogen and dipole-dipole bonding interaction. Such interactions can occur in pristine and modified clays, through the OH groups of polymer with Si-O-Si and OH groups of clay, creating the process of exfoliation. The increase in mechanical properties of PVA/MMT nanocomposites respect to neat PVA, suggested also the possibility of interactions between the inorganic layers and PVA. The increase in interlayer spacing of modified clays (MMT$_{\text{TEA}}$ and MMT$_{\text{HDTMA}}$) indicated the possibility the reaction with PVA.

Summarizing the clay nature in the polymer matrix affects both the structure and the tensile properties of the polymer/clay nanocomposites.

Referencias Bibliográficas