

# Preparation and Characterization of Pure PVA and PVA/MMT Matrix: Effect of Thermal Treatment

Albana Hasimi, Edlira Tako, Partizan Malkaj, Elvin Çomo, Blerina Papajani, Mirela Ndrira, Ledjan Malaj

**Abstract**—Many endeavors have been exerted during the last years for developing new artificial polymeric membranes, which fulfill the demanded conditions for biomedical uses. One of the most tested polymers is Poly(vinyl alcohol) [PVA]. Our teams are based on the possibility of using PVA for personal protective equipment against COVID-19. In personal protective equipment, we explore the possibility of modifying the properties of the polymer by adding Montmorillonite [MMT]. Heat-treatment above the glass transition temperature is used to improve mechanical properties mainly by increasing the crystallinity of the polymer, which acts as a physical network. Temperature-Modulated Differential Scanning Calorimetry (TMDSC) measurements indicated that the presence of 0.5% MMT in PVA causes a higher T<sub>g</sub> value and shaped peak of crystallinity. Decomposition is observed at two of the melting points of the crystals during heating 25-240 °C and overlap of the recrystallization ridges during cooling 240-25 °C. This is indicative of the presence of two types (quality or structure) of polymer crystals. On the other hand, some indication of improvement of the quality of the crystals by heat-treatment is given by the distinct non-reversing contribution to melting. Data on sorption and transport of water in PVA films: PVA pure and PVA/MMT matrix, modified by thermal treatment are presented. The membranes become more rigid as a result of the heat treatment and because of this the water uptake is significantly lower in membranes. That is indicated by analysis of the resulting water uptake kinetics. The presence of 0.5% w/w of MMT has no significant impact on the properties of PVA membranes. Water uptake kinetics deviate from Fick's law due to slow relaxation of glassy polymer matrix for all types of membranes.

**Keywords**—Crystallinity, montmorillonite, nanocomposite, poly(vinyl alcohol).

## I. INTRODUCTION

GLOBAL concerns caused by the recent respiratory coronavirus disease (COVID-19) urged the widespread use of personal protective equipment (PPE) by people around the globe. These include face masks, gloves, gowns, aprons, hoods, eye-shields, and shoes covers [1]. Using biodegradable precursors along with such multifunctional properties may be a new approach for controlling the pandemic while caring for our planet and people. Researchers are focusing on the general filtration mechanisms, manufacturing technologies used to make face mask media, characterization of different surgical face mask structures, biodegradable materials that have been used, desired added functionalities, and the future demands for

such effective biodegradable multifunctional face masks.

Hydrogels are vastly hydrophilic macromolecular networks, which are produced by chemical or physical crosslinking of soluble polymers. The peculiar properties of hydrogels, such as high sensitivity to physiological environments, hydrophilic nature, soft tissue-like water content and adequate flexibility, make them excellent candidates for biomedical applications. Hydrogels can swell and de-swell water in a reversible direction, showing specific environmental stimuli-responsive e.g., temperature, pH, and ionic strength [2], [3]. Biomaterial researchers have been very interested in polymeric hydrogels for a long time. Following the revolution in hydrogel appearance, it became simpler to manufacture wound dressings employing active and functional materials rather than passive ones. The following explanations were used in the initial attempts by biomaterial scientists to argue that hydrogels as dressing membranes meet all standards for wound healing and are suitable candidates for burn victims in the quickest period possible: (1) Hydrogels regulate the body's lost liquids and fluids, (2) they keep the wound area moist and wettable, and (3) they have a structure and compatibility similar to tissue [2]. The only disadvantage of hydrogels is their poor mechanical stability at swollen state. This drawback has been addressed by using “composite or hybrid hydrogel membranes” system consisting of more than one polymer in the dressing composition [1].

PVA is a polymeric hydrogel with a low-toxicity biocompatible polymer, suitable for a wide range of biomedical applications including controlled release systems, arthroplasty and tissue engineering [3], [4]. As with other hydrophilic polymers, various methods are used for creating a three-dimensional polymer network in order to limit dissolution in water, to improve the mechanical properties and to modify the kinetics and equilibrium water uptake properties of the polymer as well as the drug release profiles, employing the dressing's composition for a mask on the face [5]. Over half a century, PVA is one of the most studied and used polymers. Due to its tunable physicochemical properties, structural versatility, reusability and selectivity, studies have been conducted on the potential use of PVA as an absorbent compared to traditional adsorbents such as clay and activated carbon [6]. Much information is available in the literature on dye adsorption

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studies using PVA and PVA-based polymer composite adsorbents [6]. Also, the ability to produce PVA/MMT matrices is reported by different researcher groups [7]. The ability to modify PVA property with an Albanian MMT nanoclay is also focused on this work.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

PVA by Aldrich (cat.No 36313-8) with 98–99% hydrolyzed and Mw = 31–50 K in the form of powder was supplied [8].

The basic raw material used in producing nanoclay is Montmorillonite (MMT) [9]. It can be chemically described, as hydrated sodium calcium aluminum magnesium silicate hydroxide  $(\text{Na}_{0.42}\text{K}_{0.09}\text{Mg}_{0.034}\text{Ca}_{0.009})(\text{Fe}^{3+}_{1.26}\text{Al}_{0.45}\text{Mg}_{0.24}\text{Fe}^{2+}_{0.006})(\text{Si}_{13.69}\text{Al}_{0.30})\text{O}_{10}(\text{OH})_2$  [10]. The interaction between nanoclay particles and polymer matrix significantly depends upon the hydroxyl groups and charges present in the nanoclays particle.

### B. Preparation of PVA and PVA/MMT Films

Aqueous PVA solutions (10% wt) were prepared by dissolving the polymer powder in deionized water at 90 °C for 6 h under magnetic stirring. In the case of PVA/MMT films, the 0.05%wt MMT was added to the PVA solution, under magnetic stirring for 24 h. Pure PVA films are obtained in Petri dishes by evaporation under atmospheric conditions of the water of the solution, which has been allowed to cool beforehand. Rectangular samples with thicknesses of  $200 \mu\text{m} \leq 2L \leq 550 \mu\text{m}$  were cut and either (i) kept in the desiccator until use (as-prepared films) or (ii) heated for 20 min at 130 °C (i.e. at a temperature between the glass transition and melting temperature) and subsequently transferred in a desiccator (thermally treated films) [8].

### C. Thermal Analysis

Temperature modulated DSC (TMDSC) measurements on solute PVA samples of 5–12 mg were performed with model DSC 250 with RCS90 of TA Instruments, using a heating rate of 10 °C/min and a temperature modulation of  $\pm 0.80$  °C every 60 s, under nitrogen flow at a flow rate of 30 mL min<sup>-1</sup>. The degree of crystallinity of the sample was determined from the total DSC signal during a first heating run from 25 °C to 250 °C. After cooling, with the same rate, to 25 °C, a second run was performed for the determination of the inflection point of glass transition (T<sub>g</sub>) from the reversing TMDSC signal. All measurements were performed at least three times for each matrix.

### D. FTIR Measurements

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the materials. PVA films and PVA/MMT matrix hydrogels were obtained as thick films and analyzed by FTIR using Absorbance Mode. A Bruker Alpha II FTIR spectrometer with a Diamond Crystal ATR were utilized. Broadly speaking, ATR simply light through a crystal onto the sample being examined. Light interacts with the sample, re-transmits through the crystal and

is detected. Due to the way ATR is performed, there is a slight difference between the spectrum obtained with ATR and the spectrum obtained with transmission. In ATR the IR light is refracted, and different wavelengths of IR light get refracted slightly differently. This allows some wavelengths of IR light to penetrate deeper into the sample than others. However, in transmission, the IR light travels straight through the sample, so the penetration depth of different wavelengths of IR light has no effect on the spectrum. Diamond, on the other hand, is an excellent all-purpose material as it is suitable for almost all specimens. Diamond is extremely hard and chemically inert, making it highly resistant to chemical and physical damage.

### E. Water Uptake Measurements

Initially dry, rectangular matrix of lateral dimensions  $1.2 \times 2.0$  cm<sup>2</sup>, were immersed in a thermostated water bath ( $25 \pm 0.2$  °C) and periodically taken out, blotted, and weighed. Each experiment was run at least three times [11], [12].

## III. RESULTS AND DISCUSSION

### A. Thermal Properties

The total DSC signals during the first heating run of pure PVA and of PVA/MMT samples are shown in Fig. 1. The reversing signal of the 2nd heating run is used for the T<sub>g</sub> determination. Heat-treatment enhances crystallinity (examples shown in Table I) without materially affecting the T<sub>m</sub> ( $186.4 \pm 5.33$  °C) or the T<sub>g</sub> ( $72.9 \pm 0.81$  °C) of the polymer (Fig. 1).

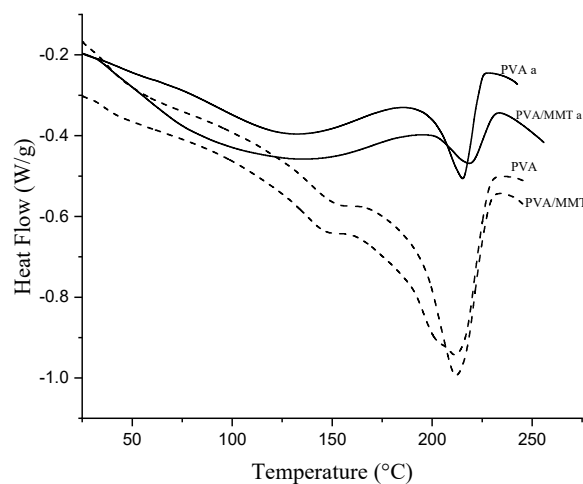


Fig. 1 Total, DSC signal during the first (up to 250 °C) spectra of as-prepared (---) and thermal treatment (—) of PVA and PVA/MMT matrix

On the other side, the distinct contribution to melting, which is represented in the melting peaks becoming deeper and sharper, may be a sign that the quality of the crystals has improved by heat treatment [8]. The semi-crystalline structure of samples was confirmed by the X-ray diffractograms (results not shown here).

Regarding the effect of the presence of MMT, we observed that it spoils the quality of the crystals: indicated by relatively broader melting endotherm, however the degree of crystallinity

of PVA is not materially disturbed (examples shown in Table I).

### B. Characterization by FTIR Spectroscopy

As shown in Fig. 2 the only distinct difference in the IR

spectra of the thermally treated film, as compared to the as-prepared film, is the intensification of the  $1142\text{ cm}^{-1}$  peak due to the increased crystallinity of the former sample [8] (shown by arrows in Fig. 2).

TABLE I  
 EFFECT OF HEAT-TREATMENT, AND THE PRESENCE OF MMT ON THE PROPERTIES OF PVA

Sample	As prepared				Thermal-treatment			
	Tg (°C)	Crystallinity (%)	Tm (°C)	Q <sub>w∞</sub> (g/g)	Tg (°C)	Crystallinity (%)	Tm (°C)	Q <sub>w∞</sub> (g/g)
PVA	73.98 ± 0.72	34.46 ± 2.05	186.17 ± 1.97	2.05 ± 0.18	72.03 ± 0.82	55.55 ± 1.53	179.01 ± 1.92	0.63 ± 0.23
PVA/MMT	72.77 ± 0.86	26.84 ± 3.72	190.75 ± 3.89	1.96 ± 0.16	73.10 ± 0.94	48.56 ± 2.19	189.85 ± 2.15	0.96 ± 0.14

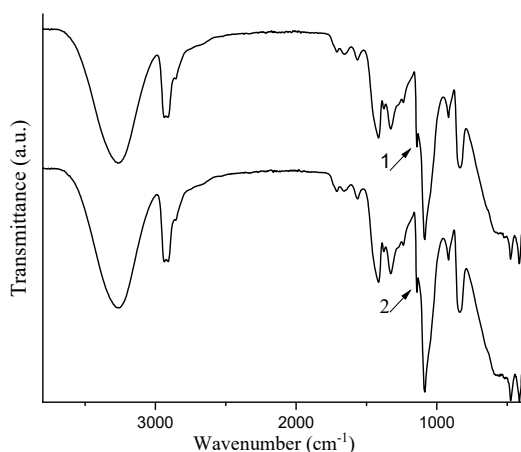


Fig. 2 IR spectra of as-prepared (1) and thermally treated (2) PVA films; the difference in intensification of the  $1142\text{ cm}^{-1}$  peak is shown by arrows nonlinear data to a higher dimensional feature space

The intensity of the  $1142\text{ cm}^{-1}$  peak is influenced by the crystalline portion of the polymeric chains. According to the literature [13]-[16], this peak is related to the symmetric C-C stretching mode or stretching of the C-O of a portion of the chain where an intramolecular hydrogen bond is formed between two neighboring OH groups that are on the same side of the plane of the carbon chain [14].

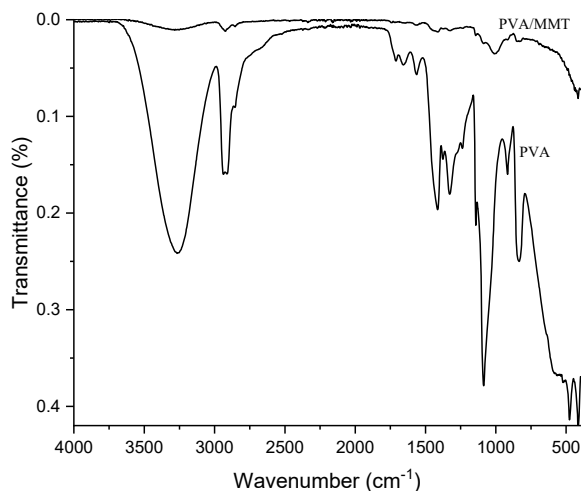


Fig. 3 IR spectra of as-prepared PVA and PVA/MMT matrix

The presence of MMT makes the PVA films opaque, and therefore the transmittance decreases significantly, as shown in Fig. 3. Analyzing the IR spectra of PVA/MMT matrix, we observed that the main characteristic of peaks is like in the pure PVA films. This is also confirmed by Fig. 4, which shows a sample of the IR spectrum of PVA/MMT with and without thermal treatment. So, for the studied concentration (0.5MMT w/w polymer), no fundamental changes were found.

Thus, other factors, in conjunction with the increase of total crystallinity, must be taken into consideration in order to account for the said reductions in swelling ability of the polymer in water [8].

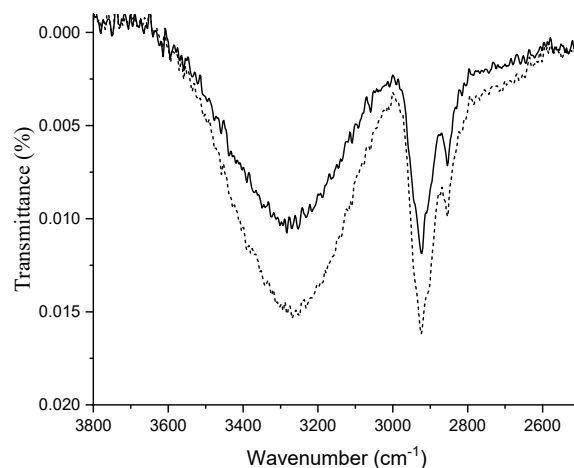


Fig. 4 IR spectra of as-prepared (—) and thermally treated (....) PVA/MMT matrix

### C. Water Uptake

Representative water sorption kinetic measurements in PVA films are shown in Fig. 5 on a plot of the amount of water uptake  $Q_{wt}$  ( $\text{g H}_2\text{O/g PVA}$ ) vs  $t^{1/2}/L$ . Analogous data on the effect of MMT are presented also in Fig. 5. The corresponding equilibrium values  $Q_{w\infty}$  are listed in Table I.

It is clearly expressed in Fig. 5 that the water kinetics are close to the Fick kinetics, but with discrepancies that require more in-depth study. Over and above that we have no significant effects regarding the heat treatment or the presence of MMT in both categories of matrix (with and without heat treatment). On the other hand, when we measure the amount of absorbed water, we notice that the heat treatment has a

remarkable effect, as shown in Fig. 6 and Table I. However, this has not been the case of the presence of MMT, which apparently does not affect the quality of matrix.

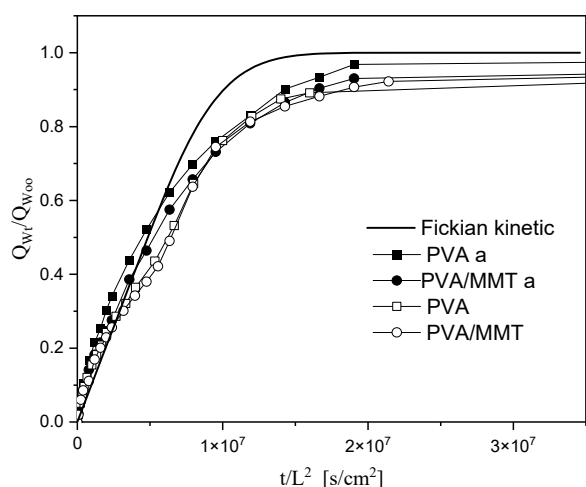


Fig. 5 Fractional water uptake kinetics in as-prepared (full points) and thermally treated (open points) PVA films (■, □) and PVA/MMT matrix (●, ○) vs Fickian kinetic. The thickness  $2L(\mu\text{m})$ : 500-550. The lines are drawn to aid the eye

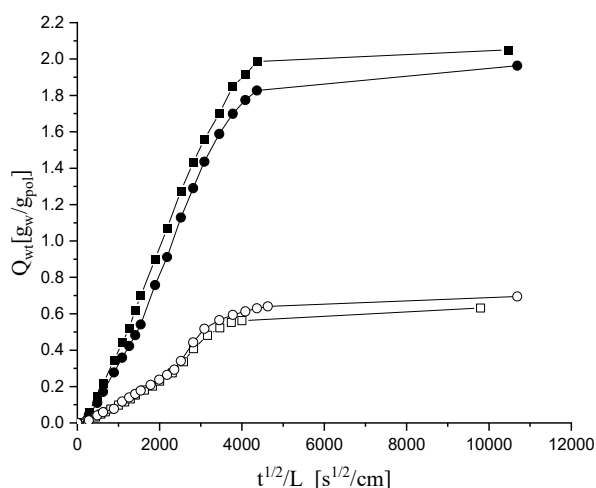


Fig. 6 Representative results on the effect of thermal treatment: Water uptake kinetics in as-prepared (full points) and thermally treated (open points) PVA films (■, □) and PVA/MMT matrix (●, ○) thickness  $2L(\mu\text{m})$ : 500-550. The lines are drawn to aid the eye

#### IV. SUMMARY AND CONCLUSIONS

In the present work, the transport properties of water in PVA films and modified by adding Albanian MMT or thermal treatment above  $T_g$  were systematically studied.

Comparatively we found that the presence 0.5% w/w of MMT has no significant impact on the properties of membranes. Because of thermal treatment the films become more rigid and because of this: the water uptake is significantly lower in membranes. Also, the water uptake kinetics deviate slightly from Fick's law due to slow relaxation of glassy polymer matrix. Thermal treatment has the same effect on

membranes with MMT, as in pure PVA.

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