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Effect of trifluoroacetic acid on the properties of polyvinyl alcohol and polyvinyl alcohol–cellulose composites

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HIGHLIGHTS

- A polyvinyl alcohol reinforcement process with amorphous cellulose is demonstrated.
- PVA–cellulose composites have been synthesized using trifluoroacetic acid (TFA).
- TFA treated PVA films demonstrate exceptional strain at break values around 700%.
- Trifluoromethyl groups induce a certain degree of water resistance.

GRAPHICAL ABSTRACT
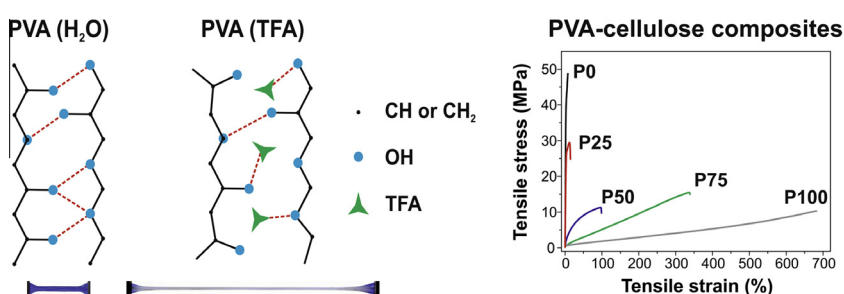
ARTICLE INFO

ABSTRACT

Highly stretchable polyvinyl alcohol (PVA) films with a strain at break of around 700% were obtained from solutions in trifluoroacetic acid (TFA). Structural and chemical analysis by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (ATR–FTIR) showed that TFA is retained by PVA via hydrogen bonds between the carboxylic acid groups and the hydroxyl groups of the polymers causing a strong plasticizing effect. Additionally, composites of PVA with cellulose could be developed using TFA as common solvent. The morphological and mechanical properties of the polymer composites could be accurately tuned by modifying the relative concentrations of the two polymers. Data from water adsorption isotherms and wetting measurements indicated that the presence of trifluoromethyl groups in PVA render the composite films relatively hydrophobic.

1. Introduction

Since the middle of the 20th century, the rapid development of the fossil fuel-based plastics industry has led to extensive use of conventional plastics in many sectors. However, it is now well acknowledged that increasing consumption of fossil fuel-based plastics causes very serious environmental problems such as land and water pollution, bioaccumulation, recycling and greenhouse effects [1–3]. As such, the worldwide interest in replacing fossil fuel-based plastics with natural and biodegradable polymers has

grown tremendously. For instance, according to *Web of Science* by *Thomson Reuter's* data compiled by Chen and Martin, the number of citations on publications related to bio-based polymers and applications has increased exponentially in the last decade [4]. One important strategy to reduce the impact of petroleum based plastics has been the formation of composites with natural polymers. For example, composites from polyethylene and polypropylene with cellulose fibers have received intensive research [5,6]. However, this approach has been proven to be insufficient in terms of environmental sustainability. Alternatively, synthetic polymers with biodegradable backbones like polyvinyl alcohol (PVA) have been investigated as potential matrix for fully biodegradable composites [7,8]. PVA is the most widely produced biodegradable synthetic polymer that is also water-soluble. It is a semicrystalline polymer having nontoxic, transparent and biocompatible properties [9]. Additionally, PVA has good chemical resistance and physical attributes, such as film forming ability, emulsification and adhesive properties [10]. Hence, PVA is used in a broad spectrum of applications such as tissue scaffolding [11,12], filtration materials and membranes [13–15], wound dressing and drug release [16,17], food packaging [18] and adhesion industry [10]. The relatively poor mechanical strength and structural integrity of PVA are usually improved with reinforcing agents. One of the most used is cellulose in the form of microfibrillated cellulose [8], nanowhiskers [9,19], nanofibers [20], or nanoparticles [21]. Additionally, good miscibility between cellulose and PVA has been described in literature resulting in the preparation of blends by using *N,N*-dimethylacetamide-lithium chloride as solvent [22,23]. The interaction between both polymers through hydrogen bonds of hydroxyl groups has been proposed as the driving force for the formation of such blends.

Cellulose is the most abundant natural biopolymer in the world. It is found in the plant cell walls, including marine algae, tunicates and some bacteria to which it provides physical structure and strength [24]. Cellulose consists of a linear chain of several $\beta(1 \rightarrow 4)$ linked D-glucose units and has a number of important properties such as complete biodegradability [24], light weight [25] and good mechanical strength [26,27]. Cellulose fibers are commonly used in various technological products such as packaging paper, membranes, medical products, textiles, etc. [28]. Cellulose is dissolved by few substances, such as aqueous alkali solutions, aqueous complex solutions, ionic liquids, *N,N*-dimethylacetamide-lithium chloride, *N*-methylmorpholine *N*-oxide and strong acids [29]. Specifically, trifluoroacetic acid (TFA) has been shown to solubilize cellulose and related compounds [30,31] and various agricultural plant wastes [32] by reacting with hydroxyl groups and formation of the corresponding trifluoroacetate derivatives [33]. This causes the breakage of the intermolecular hydrogen bonding network [34]. TFA is an organic acid, volatile, potentially recyclable by distillation [35] and miscible with many organic solvents as well as water [32]. TFA can also dissolve many other synthetic polymers such as acrylics and PVA [36,37].

In this study, we present a direct and simple method to produce novel PVA–cellulose plastics by blending them in TFA. Many properties associated with both amorphous cellulose and PVA can be incorporated into the plastics by simply controlling their relative concentrations. Furthermore, we show that TFA not only solubilizes PVA but also acts as a plasticizer.

2. Materials and methods

2.1. Materials

High purity microcrystalline cellulose (crystallinity ~79%) from cotton linters, polyvinyl alcohol (PVA) (typical average M_w 85,000–124,000 and 98% hydrolyzed), and anhydrous trifluoroacetic acid (TFA) were purchased from Sigma Aldrich and used as received.

2.2. Preparation of the composites

PVA–cellulose films were prepared by mixing cellulose and PVA solutions in TFA. Cellulose solutions with a concentration of 1 wt.% were prepared by dissolving microcrystalline cellulose powder in TFA. The complete dissolution took three days under ambient conditions. Similar solutions were prepared with PVA in TFA. PVA flakes dissolved in three hours. Films were prepared by mixing predetermined volumes of above solutions in order to obtain various concentrations of PVA in the plastics on dry basis, namely, 0, 12.5, 25, 37.5, 50, 62.5, 75, 87.5 and 100 wt.%. Samples were named as P0 (pure cellulose), P12.5, P25, P37.5, P50, P62.5, P75, P87.5 and P100 (pure PVA) according to the concentration of PVA. A control sample of PVA was also prepared by dissolving it in water at a concentration of 1 wt.% (P100w). All samples were stored at 44% RH for 7 days before analysis to ensure the reproducibility of the measurements.

2.3. Morphological characterization

The morphology of the PVA–cellulose films was characterized by scanning electron microscopy (SEM), using a JEOL JSM-6490LA microscope working in high vacuum mode, with an acceleration voltage of 15 kV. The particle diameter (as a result of phase separation) and surface density of the films' surface were calculated with ImageJ image analyzer program. SEM images were used to measure both diameter and number of particles. Basically, the images were loaded into the software and diameter of the particles was measured using a two point measuring analysis. For the particle count, highly contrasted images were used. Approximately, 100 measurements were taken to obtain each diameter and density distributions.

Fluorescence photomicrographs were obtained with a fluorescence optical microscopy Nikon Eclipse 80i using filters 480/30 for the excitation and 550/60 for the emission modes. A magnification of 40× was used for all micrographs.

2.4. Chemical and structural characterization

Infrared spectra were obtained with an attenuated total reflectance (ATR) accessory (MIRacle ATR, PIKE Technologies) coupled to a Fourier transform infrared (FTIR) spectrometer (Equinox 70 FT-IR, Bruker). All spectra were recorded in the range from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}, accumulating 128 scans.

The crystallinity of the films was analyzed by X-ray diffraction (XRD) using a diffractometer Rigaku SmartLab X-ray Diffractometer equipped with a copper rotating anode. The X-ray source was operated at 40 kV and 150 mA. A Gobel mirror was used to obtain a parallel beam and to suppress Cu Kβ radiation (1.392 Å). The measurements were performed using a 2θ scan. Diffractograms were deconvoluted using PeakFit software. The degree of crystallinity of the PVA–cellulose blends was determined with Eq. (1) as follows [38]:

$$CrI = (A_{cr} - A_{am})/A_{cr} \times 100 \qquad (1)$$

where *CrI* is the crystallinity index in percent, A_{cr} is the peak area of all the crystalline peaks and A_{am} is the peak area of the amorphous contribution.

Wide angle X-ray scattering (WAXS) curves were obtained using a Rigaku SmartLab X-ray diffractometer. The data were taken in the scattering range from 2θ = 5° to 60°. Ni-filtered Cu Kα radiation was used in all cases.