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Influence of nanodiamond loading on properties of poly(vinyl alcohol) nanocomposite membranes.

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Abstract. Carbon nanomaterials are well-known for their unique physical properties. They have attracted interest as reinforcing fillers because of their superb mechanical properties. We report the excellent reinforcement properties of polymer nanocomposites by the incorporation of nanodiamond (ND). ND has been expected to offer polymer nanocomposites optimal properties because of its smooth surface and excellent optical, mechanical, and thermal properties, which can approach the values of single diamond crystal. We prepared advanced nanocomposites membranes based on poly(vinyl alcohol) (PVA) and ND in a single step using the solution casting method from aqueous medium and achieved the high dispersibility of ND in the PVA matrices. The thermal, mechanical and rheological properties of the membranes were investigated by means of thermogravimetry (TGA), dynamic mechanical analysis (DMA) and Ares G2 rheometer. The resulting nanocomposites had excellent properties derived both from ND and PVA. Thermal and mechanical properties increased dramatically with increasing ND content, indicating a strong interaction between ND and PVA. We anticipate that ND will be able to compete as a nano filler against conventional carbon-based nano fillers for polymer composites, and it is possible their reinforcement properties will be extended in the future.

1. Introduction

Polymer nanocomposites have attracted much attention not only in scientific fields but also in industrial applications due to the excellent abilities of nano-sized fillers. Nanocomposites have been reported to provide remarkable improvements in materials properties, including mechanical, thermal, and barrier properties, compared with those of polymer itself and micro-sized fillers composites.^[1] Carbon-based nanomaterials are well-known for their incredibly high mechanical properties, and they have attracted interest as reinforcing fillers for polymer nanocomposites.^[2] In recent years, NDs has been produced by several procedures, such as detonation shock-wave synthesis (from various starting materials), and it has been exploited in vast fields of nanotechnology.^[3] In this work, we selected PVA, a watersoluble and biodegradable polymer, as a polymer matrix. PVA membranes are applied in many fields, especially in organic/inorganic separations, pervaporation, biomedical applications, catalysis, controlled drug release.^[4-6] We prepared PVA+ND nanocomposites by single-step solution casting method from an aqueous suspension, and we investigated the structure and thermo-mechanical properties of the nanocomposites.



2. Experimental

2.1. Material

PVA (hydrolyzed 99+%, $M_w = 86000\text{--}98000$) was obtained from Sigma-Aldrich (USA). Powder of grade G01 detonation nanodiamonds (NDs) was purchased from PlasmaChem GmbH. All the chemicals were of analytical grade and used as received. Deionized water was utilized for all the membrane preparation experiments.

2.2. Membrane preparation

Nanocomposite PVA membranes were prepared using a solution casting method. Surface of NDs have been modified via thermal treatment in air atmosphere to provide them negatively charge nanodiamonds (NDs⁻), which were obtained by annealing at 450 °C for 5 h. Then, the annealed NDs⁻ powder was dispersed in deionized water (DI) at different concentration from 0.05 to 1.9 %, expressed as weight percent in mentioned solvent (Figure 1). As a polar protic solvent was used DI with resistivity 14.3 MΩ·cm at 25°C. Bandelin Sonopuls - Ultrasonic homogenizer HD 3200 was applied to obtain required dispersion of NDs⁻. Sonication for 3 h with continuous stirring were applied to acquire grey-colored nanodispersion. Afterwards, the solutions were centrifuged three times at 4000 rpm (2325g) for 1 hour. Next a 5 wt% solution of PVA in NDs solutions was prepared by continuous stirring at 90 °C until the complete dissolution was achieved. The prepared solution was poured into the automatic film applicator (TQC, Germany) equipped with a glass plate and was fabricated into membranes with uniform thickness and dried at 40 °C.

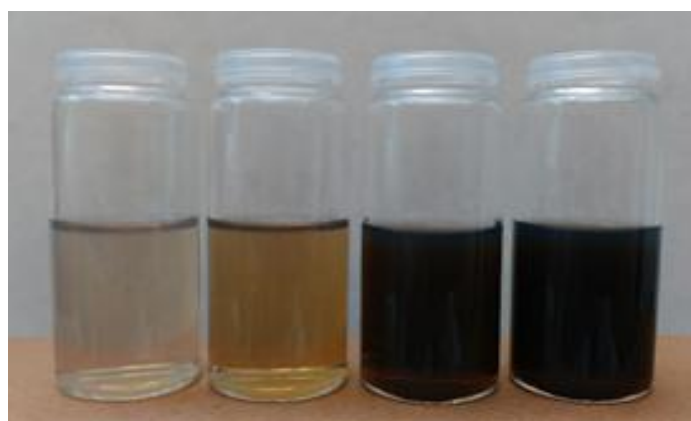


Figure 1. The visual appearance of NDs dispersions in different weight concentrations 0.05, 0.25, 1 and 1.9 wt% for DI water.

2.3. Characterization

The rheological studies of the prepared PVA and PVA+ND solutions were measured on a rheometer ARES G2 from TA Instruments. The polymer solutions were inserted between two parallel plate geometries ($d = 25$ mm). For each measurement, the shear rate from 0.1 to 100 s^{-1} , for a duration 30 s was carried out at room temperature.

TGA was used to evaluate the relative thermal stability of modified PVA membranes. The TGA curves were obtained with a TGA Q500 thermogravimetric analyser (TA Instruments, USA). Samples of about 5 mg were heated at a rate of 10 °C/min in N_2 atmosphere. The weight of the samples was measured as a function of temperature.

Tensile properties were determined by DMA using a DMA Q800 instrument (TA Instruments, USA). The initial length of the specimen was 20 mm, and the extension rate was 1 mm/min. For measurement was used room temperature.

3. Results and discussion

3.1. Rheology

The viscosity of the PVA solution changed after the incorporation of NDs⁻ (Figure 2). Viscosity increase with NDs⁻ content. At the shear rate 10 s⁻¹ the viscosity increase from ~0.5 to ~10 Pa·s for pure PVA and PVA+1.9ND, respectively. Highest viscosity for PVA+ND solutions is caused by the presence of NDs⁻ which operate as crosslinking agent (Scheme 1).^[7]

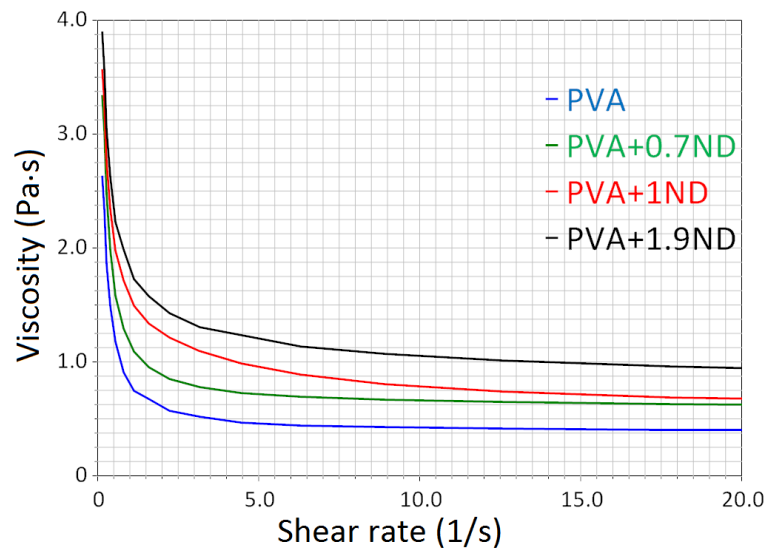
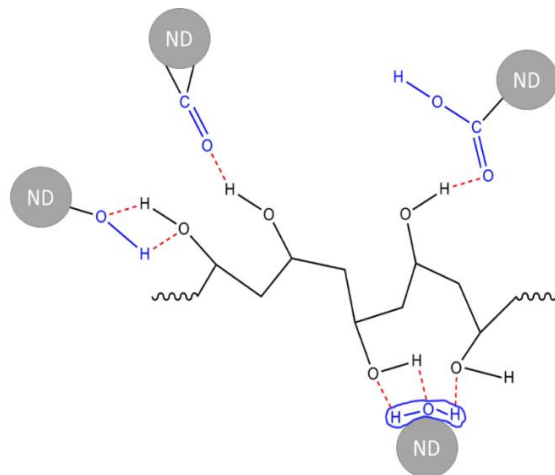


Figure 2. Rheological spectra of pure PVA solution and different NDs⁻ loadings of PVA+ NDs⁻ solutions.



Scheme 1. Schematic illustration of the interaction between PVA and NDs⁻ particles.

3.2. TGA

The TGA traces of the PVA membrane and the PVA+ND nanocomposites is shown in Figure 3. Thermal stability of nanocomposites increase with NDs⁻ content. This indicates that the nanodispersion of the NDs⁻ particles can act as a barrier to hinder the volatile decomposition products throughout the composites.^[7]

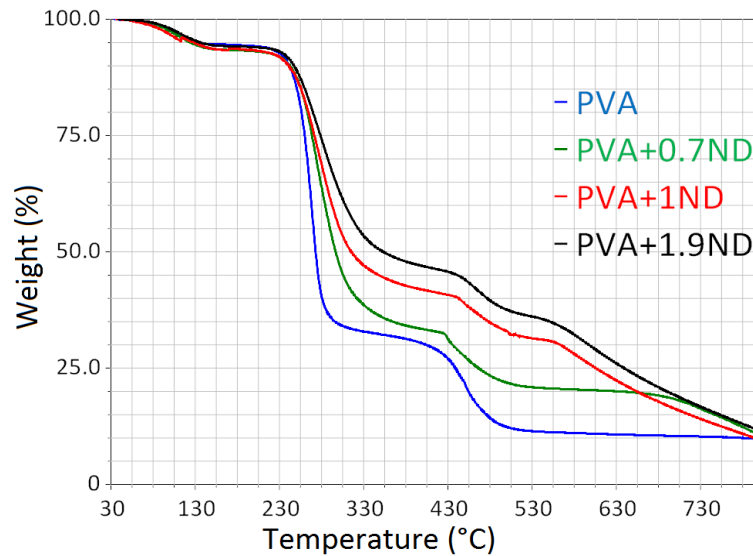


Figure 3. TGA thermograms of pure PVA and nanocomposite PVA+ND membranes.

3.3. DMA

Figure 4 shows the stress (σ) - strain (ε) curves of pure PVA membrane and the PVA+ND nanocomposites with different NDs' contents. The PVA showed the typical σ - ε curve for a conventional polymer film exposing elastic limit and maximum tensile strength (σ_{max}). σ_{max} increased drastically with the NDs' content, from 25,7 to 63,3 MPa for pure PVA and PVA+1.9ND, respectively. Thus, we can conclude that the NDs' loading clearly improved the mechanical strength of the membranes.

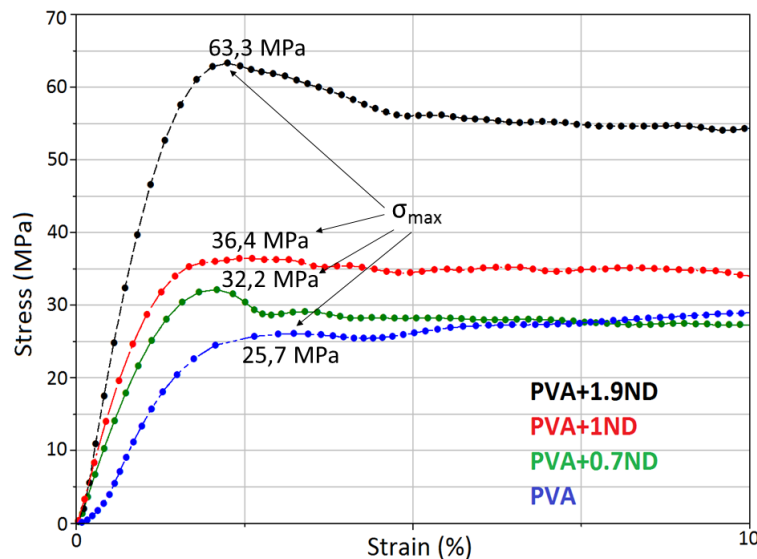


Figure 4. Stress (σ) - strain (ε) curves of pure PVA and the PVA+ND nanocomposites.

4. Conclusion

Nanodispersion of the NDs' particles in the PVA matrix was achieved by using a solution casting method from aqueous medium. The mechanical properties of the PVA+ND nanocomposites increased remarkably by the incorporation of NDs' particles. The σ_{max} values of the nanocomposites increase

with NDs content. Therefore, the ideal reinforcement effect of NDs was revealed. Thermal properties of the PVA+ND nanocomposite increased with increasing content of NDs particles. Thus, we created advanced nanocomposites by using NDs, which will be able to compete as a nanofiller against conventional nanofillers for polymer composites.

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