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Rheology Behaviour and Mechanical properties of Poly(vinyl alcohol) Membranes Modified with Nanodiamonds

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Abstract. Poly (vinyl alcohol) (PVA) membranes have found wide application in biomedicine and pharmacy for their unique properties such as biocompatibility, elasticity and the ability to absorb large amounts of water. Also carbon nanomaterials have shown great potential in a number of applications in regenerative medicine. Nanodiamonds (ND) are a unique class of carbon nanoparticles that have become known thanks to their biocompatibility, highly functional surface and unique physical, chemical and optical properties. Nanocomposite membranes based on PVA and ND were prepared by a solution casting method to achieve an even distribution of ND in the PVA matrix. The resulting nanocomposites have excellent properties derived from ND and PVA. The mechanical properties of the membranes improved significantly with an increase in ND, suggesting a strong chemical interaction between ND and PVA. The SEM showed a uniform distribution of ND in the PVA membrane. From the results of the work we assume that ND are a suitable nano-filler for PVA membranes. This work examines the properties of ND-reinforced PVA membranes and their potential use in biomedical applications.

1. Introduction

Poly(vinyl alcohol) (PVA) membranes or hydrogels, due to their properties, have found use in various fields such as food, textiles, stationery, and in particular biomedical and pharmaceutical industry [1-5]. Carbon-based nanomaterials are well-known for their incredibly high mechanical properties, and they have attracted interest as reinforcing fillers for polymer nanocomposites [6]. 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 [7]. In present work, we applied a sol-gel method to prepare PVA nanocomposite membranes reinforced by NDs. Incorporation of NDs to PVA matrix increase the mechanical strength of the PVA+ND membranes. Membranes with different contents of NDs were characterized by field emission scanning electron microscopy (FE-SEM), dynamic mechanical analysis (DMA) and rheology. The effect of NDs incorporation on the properties and morphology of the nanocomposite membranes was systematically investigated.

2. Experimental

2.1. Material

PVA (hydrolyzed 99+%, M_w = 86000–98000) was obtained from Sigma-Aldrich (USA). Powder of grade G01 detonation nanodimanods (NDs) was purchased from PlasmaChem GmbH. All the

chemicals were of analytical grade and used as received. Deionized water was utilized for all membrane preparation experiments.

2.2. Membrane preparation

Modification of NDs is shown in Figure 1. The surface of NDs was activated via thermal treatment (annealing at 450 °C for 3 h in air atmosphere) to provide them negative surface charge (NDs⁻). Subsequently, the annealed ND⁻ powder was dispersed in deionized water (DI) at different concentrations (Table 1), expressed as weight percent in mentioned solvent. 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 dispersion were centrifuged three times at 4000 rpm (2 325 g) for 1 hour. Nanocomposite PVA membranes were prepared using a solution casting method. 5 wt% solutions of PVA in NDs dispersion was prepared by continuous stirring at 90 °C until the complete dissolution was achieved. The prepared solutions were poured on glass plate and were fabricated by casting knife into membranes with uniform thickness and dried at 40 °C. Composition of prepared samples is shown in Table 1.
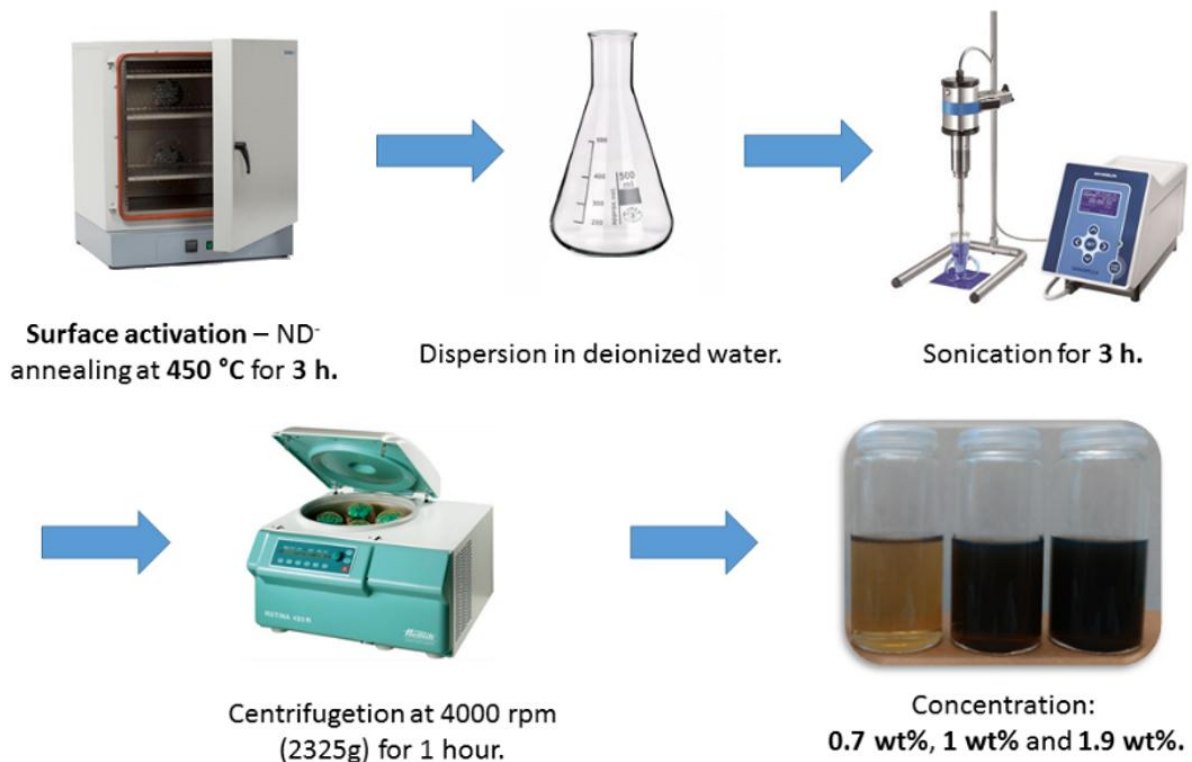

Figure 1. Surface modification of NDs

Table 1. Composition of polymer solutions

Composite designation	PVA (wt%)	NDs (wt%)
PVA	5	0
PVA+0.7ND	5	0.7
PVA+1ND	5	1
PVA+1.9ND	5	1.9

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 paralel 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.

Structure of PVA+ND membranes were investigated by Field Emission Scanning Electron Microscope (FE-SEM) JEOL JSM-7600F.

Thermo-mechanical properties were determined by DMA using a DMA Q800 instrument (TA Instruments, USA). The temperature dependence of the storage modulus was determined by DMA on the same instrument. Membrane samples with a size of 20 x 6 mm and a thickness of about 0.05 mm were used to measure the mechanical properties. Experiments were performed in N_2 atmosphere at a frequency of 1 Hz, starting from ambient temperature up to 100 °C with a heating rate of 5 °C/min.

3. Results and discussion

3.1. Rheology

The viscosity of the PVA solution changed after the incorporation of NDs (Figure 2). It is demonstrated that, viscosity increases with NDs content. At the shear rate 3 s^{-1} the viscosity increased from 0.5 to ~ 1.5 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 [8].
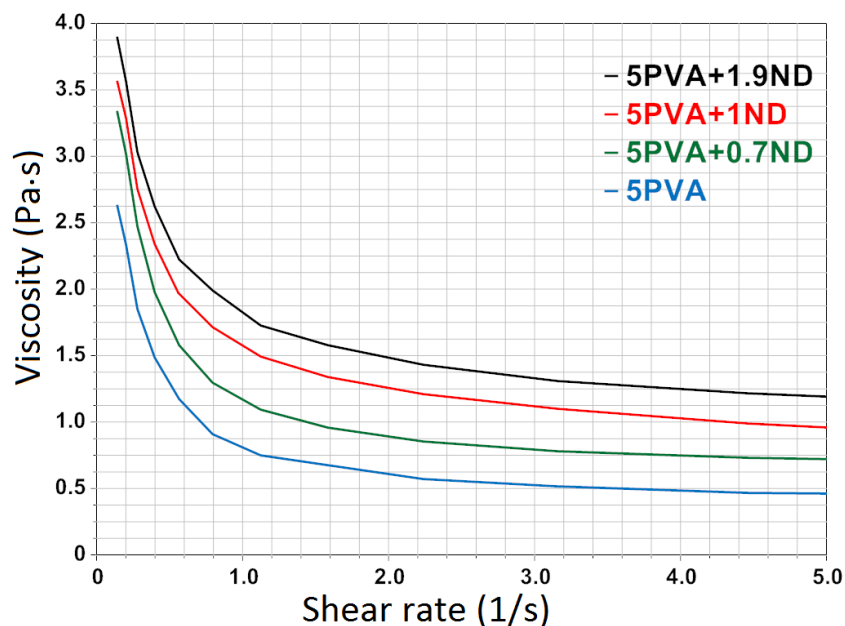

Figure 2. Viscosity behaviour of pure PVA solution and PVA+NDs solutions

3.2. FE-SEM

The morphology of PVA+ND nanocomposites were investigated by field emission-scanning electron microscopy (FE-SEM) (Figure 3). It can be seen that the ND agglomerates were well dispersed in PVA matrix. The size of agglomerates is in the range 50-150 nm.
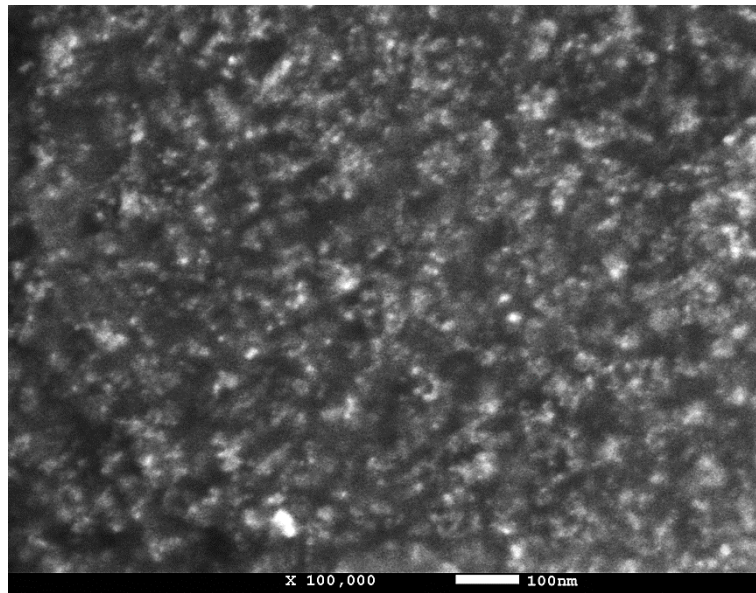
Figure 3. SEM photograph of surface of PVA+1.9ND

3.3. DMA

DMA analysis was performed to investigate the thermomechanical properties of the nanocomposite PVA membranes. The temperature dependence of the storage modulus was measured in the range from 30 to 80 °C. In the case of nanocomposites, storage modulus increased with the increasing NDs loading (Figure 4). This indicates stronger crosslinking extents for the composite membrane with NDs. A shift in the T_g temperatures towards higher values (Figure 5) indicates the reinforcement effect of ND nanoparticles. T_g based on maximum of tan delta curve shifts from 40.7 °C for PVA to 41.4, 42.7 and 44.8 °C for PVA+0.7ND, PVA+1ND and PVA+1.9ND, respectively.
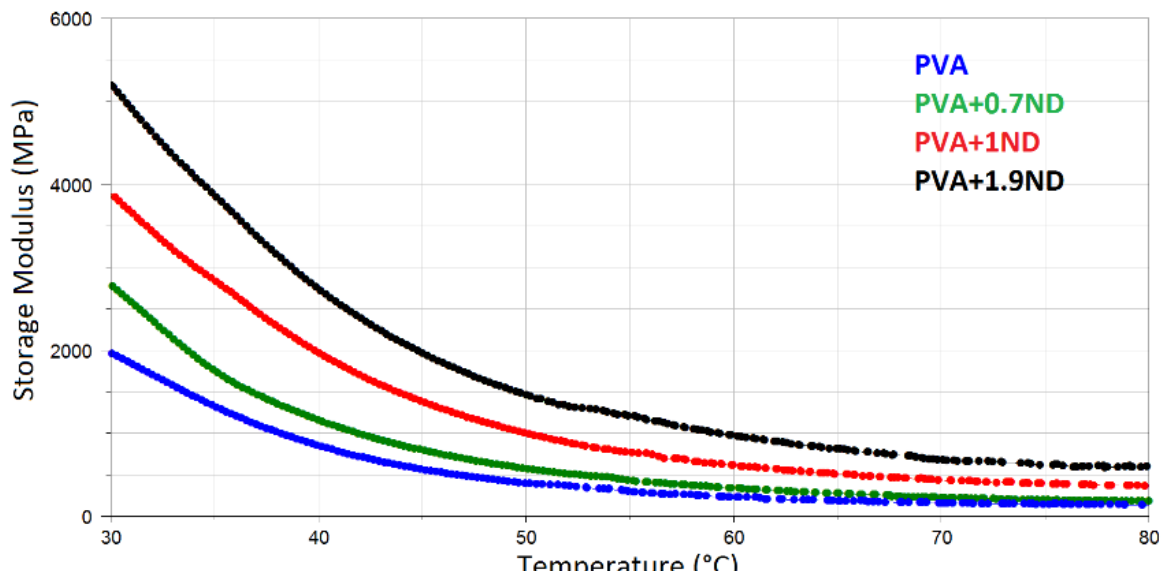

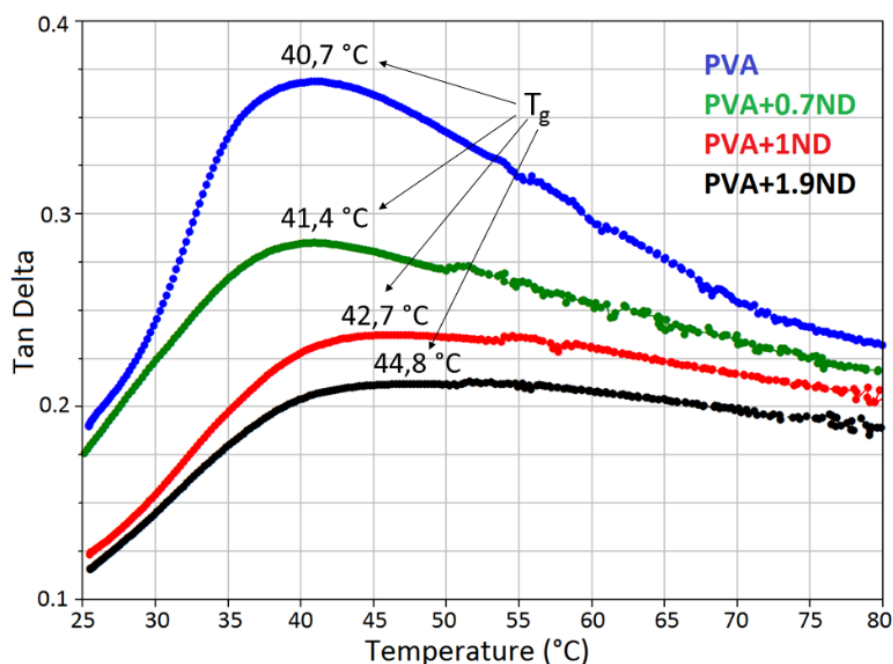**Figure 4.** Storage modulus of pure PVA and nanocomposite PVA+ND membranes

Figure 5. Tan Delta of pure PVA and nanocomposite PVA+ND membranes

4. Conclusion

Appropriate dispersion of the diamond nanoparticles in the PVA matrix was achieved by using a facile solution casting method from aqueous medium. SEM showed homogenies distribution of NDs in PVA. The mechanical properties of the PVA+ND nanocomposites increased after the incorporation of NDs. The storage modulus of the nanocomposites increase with NDs content. Hence, the favorable reinforcement effect of NDs was studied and described. Accordingly, we synthesized advanced PVA nanocomposite by using ND reinforcement, which shown a promising viscoelastic properties and gained attention for possible biomaterial applications.

Acknowledgements

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