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Nafion-based nanocomposite membranes for fuel cells

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ABSTRACT

Nafion nanocomposites were prepared with pure multiwalled carbon nanotubes (PMWCNTs), oxidised MWCNTs (OMWCNTs) and functionalised MWCNTs (FMWCNTs) as fillers, to investigate the effect of multiwalled carbon nanotubes on thermal stability, mechanical properties and electrical conductivity of Nafion membrane for fuel cell applications. The results showed an improvement on the thermal behaviour of prepared Nafion nanocomposites compared to pure Nafion with an addition of only 1 wt% MWCNTs.

INTRODUCTION

Polymer nanocomposites (PNCs) have recently shown the worldwide growth efforts in the fabrication of high temperature proton exchange membrane for fuel cells. In principle the nanocomposites are an extreme case of composite in which interface interaction between two or more phases are maximised to obtain superior performance as compared to any of the pure solid component. In PNCs, nanometer-size particles of inorganic or organic materials are homogeneously dispersed as separate particles in a polymer matrix[1]. There is a wide variety of nano-particles that are blended with Nafion to generate new structures of materials to improve its properties for proton exchange membrane fuel cell (PEMFC) applications. The current development of the PEM fuel cells is linked to the catalyst, fuels, oxidants that are being used and also to the advantages and disadvantages of Nafion under different operating conditions[2-5].

EXPERIMENTAL

The Nafion precursor (Nafion R-1100 resin) was purchased from Ion Power Inc, Bear, DE, USA. Ninety-five percent pure MWCNTs with an outside diameter of 40-60 nm, inside diameter of about 5-10 nm and a length of about 0.5-500 µm were supplied by Sigma Aldrich.

Membrane preparation

Nafion nanocomposite membranes were prepared by melt-mixing the Nafion precursor with MWCNTs at 250 °C in a Reomix OS instrument, at a rotor speed of 60 rpm for 10 min. The filler was added after two minutes of melting of Nafion inside the mixer. For each nanocomposite, the amount of MWCNTs loading was fixed to 1 wt%. Nanocomposites were prepared with PMWCNTs, OMWCNTs and FMWCNTs. The nanocomposite samples were converted into sheets or films with a thickness of about 0.12-0.2 mm using a Carver laboratory press at 2 MPa at 250 °C. The nanocomposites were then hydrolysed by immersion in a solution of 15% potassium hydroxide, 50% of deionised water and 35% of dimethyl sulfoxide at 80 °C for two hours, followed by the repeated immersion in a fresh 5M nitric acid (HNO3) solution for one hour.

RESULTS AND DISCUSSION

Morphology

The morphological orientation of MWCNTs on a polymer matrix was analysed by SEM as shown in Figure 1. The dispersion of MWCNTs is more homogeneous with oxidised MWCNTs. This homogeneous dispersion can be explained in terms of the interaction between sulfonic acid groups of Nafion and the COOH group.

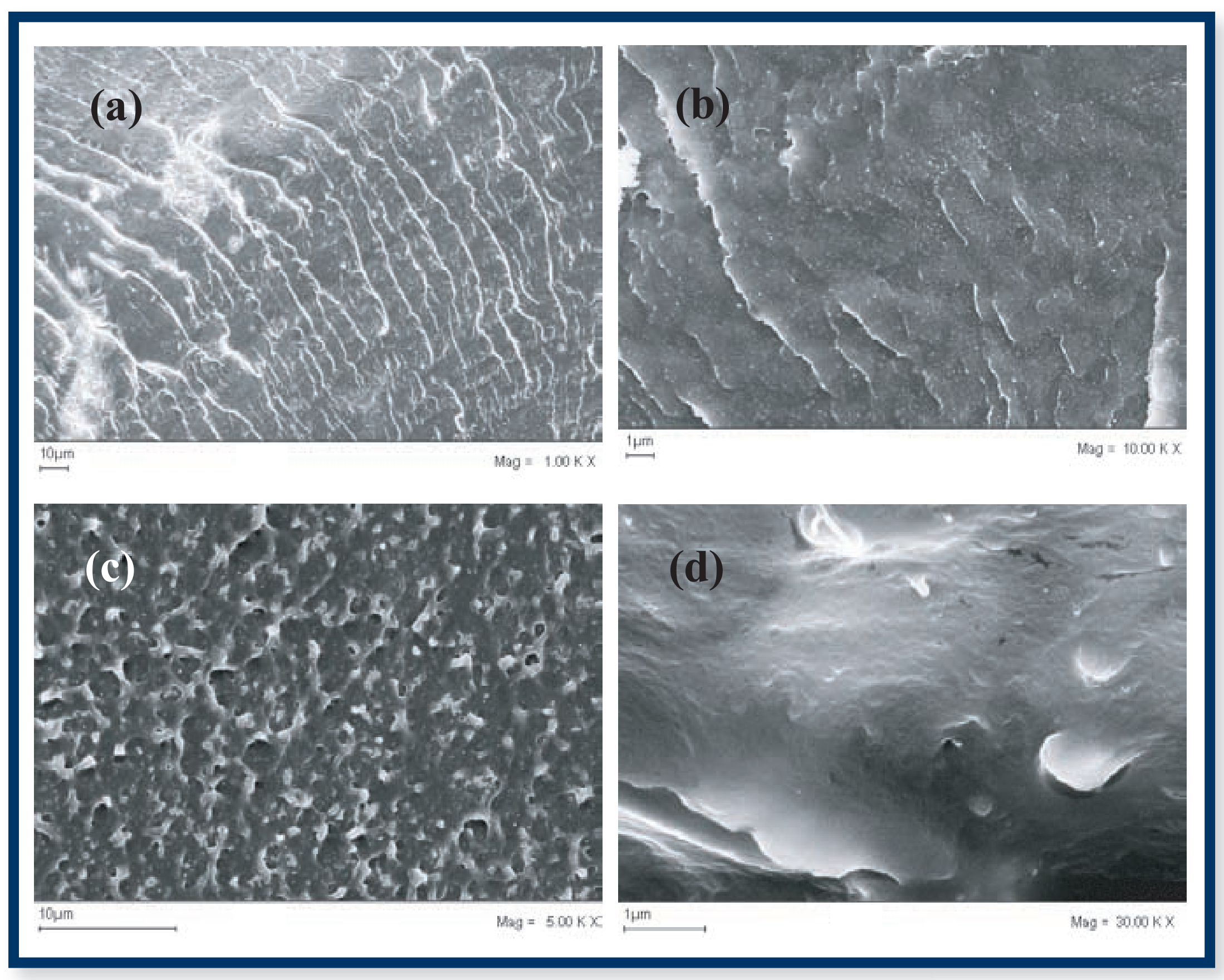

Figure 1. SEM micrographs of (a) pure-Nafion, (b) N-PMWCNTs, (c) N-OMWCNTs and (d) N-FMWCNTs

Thermal stability

The thermal stability for pure Nafion and its nanocomposites is illustrated in Figure 2. It is shown that the thermal degradation is very similar to one another. However, the onset thermal degradation (Td) temperature is different in all the nanocomposites. The weight loss at 30 – 300 °C is attributed to residual boundary water loss [5]. Nafion. TGA results shows as increase in thermal stability of Nafion after the incorporation of only 1wt% MWCNTs

Mechanical properties

DMA results in Figure 3 show the temperature dependence of tan delta for Nafion and nanocomposites. The glass transition (Tg) temperature of N/OMWCNTs nanocomposites were higher than that of pure Nafion, which is attributed to higher mechanical properties compared to other nanocomposites. This can be associated with the polarity of COOH groups, which promotes more compatibility between CNT and polymer chains. This is in agreement with a good dispersion observed by SEM.

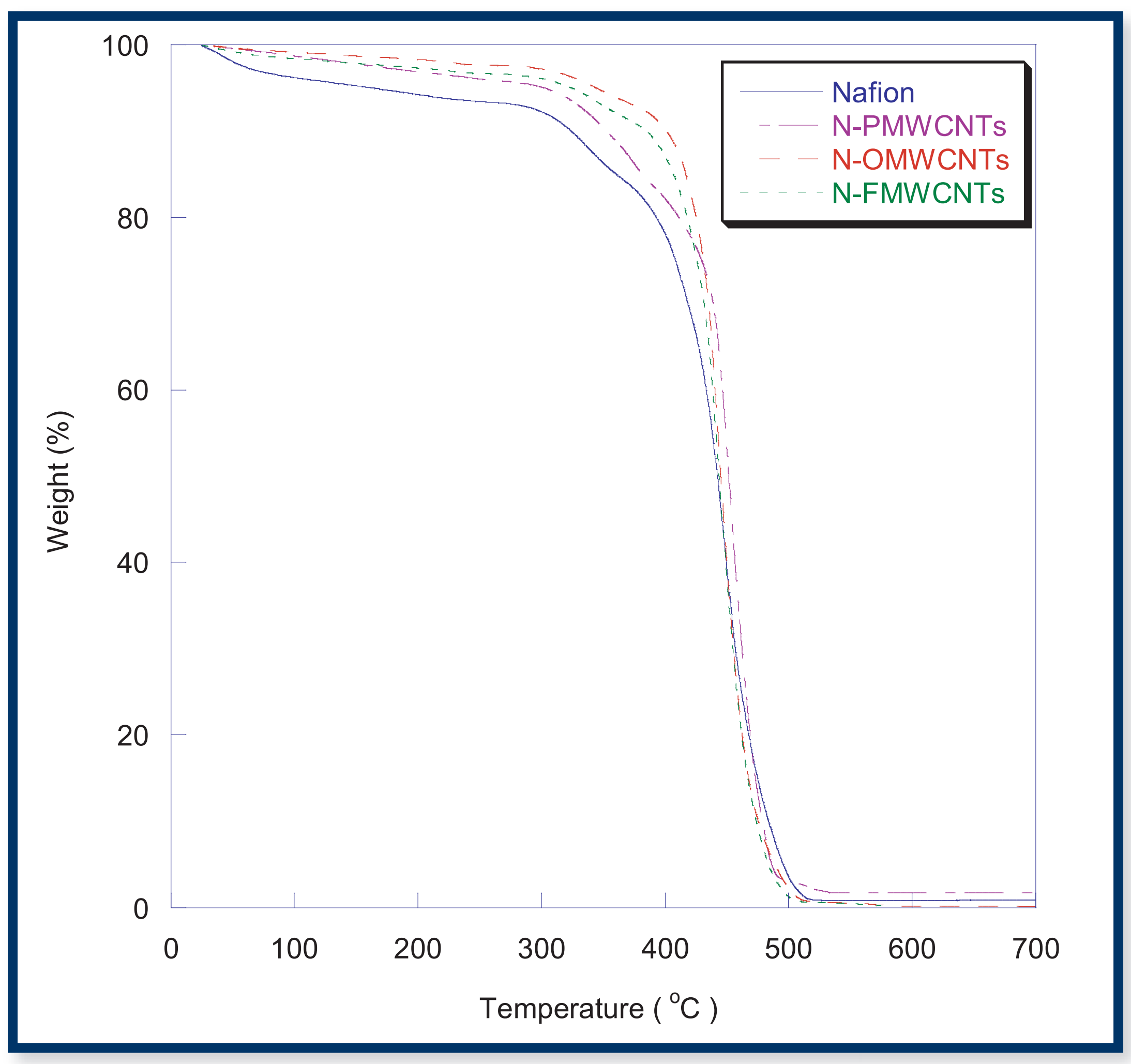

Figure 2: TGA weight loss curves of Nafion and its three MWCNT composites under oxygen atmosphere

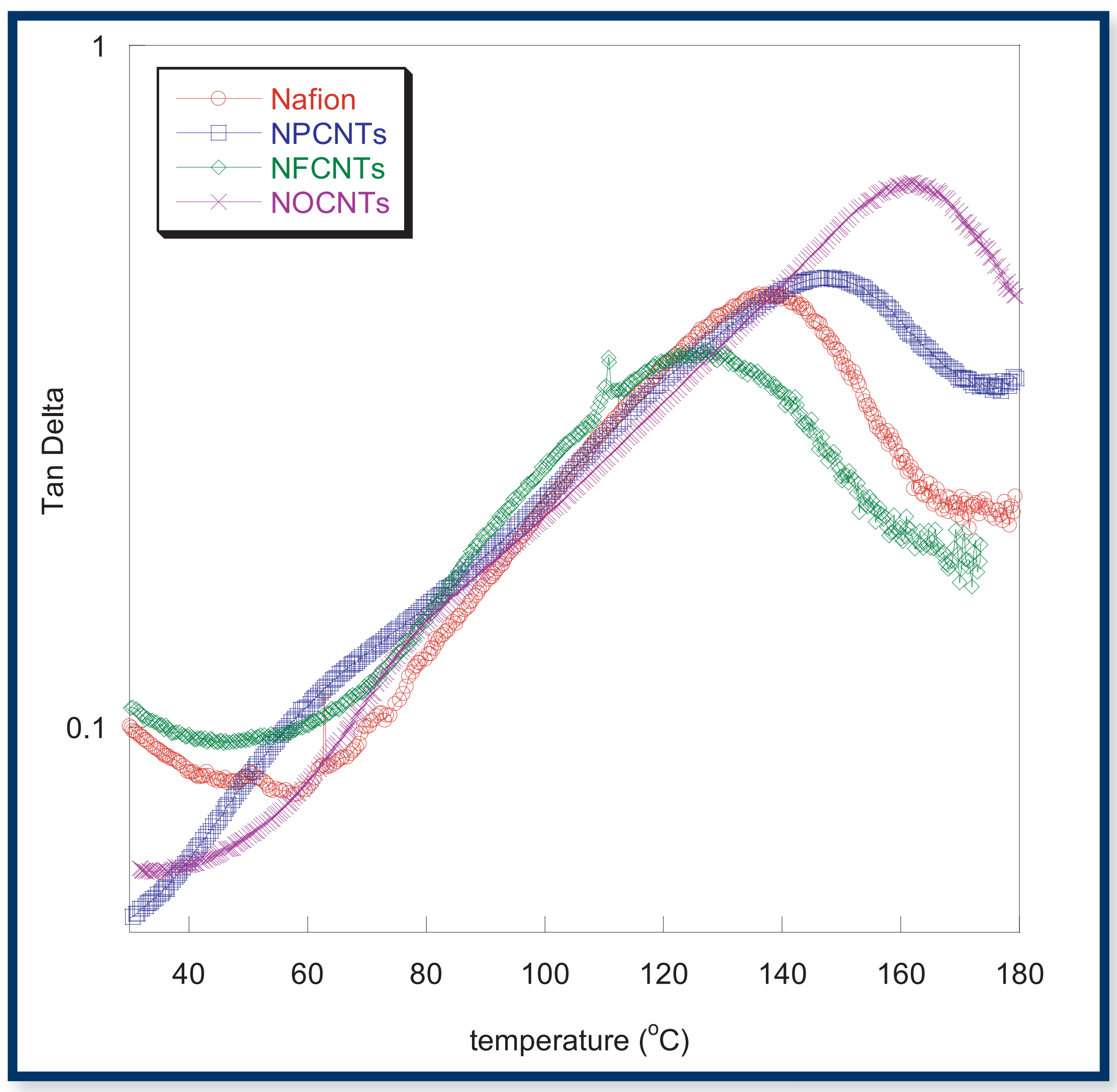

Figure 3: Temperature dependence of Tan Delta for Nafion and its MWCNT nanocomposites

Electrical conductivity measurements

The bulk resistivity changes as a function of probe spacing (0.127 cm) and is given by:

$$\rho = 2\Pi s \left(\frac{V}{I}\right) \quad \text{for } t>>s \quad \text{and } \sigma = 1/\rho$$

where s is the probe spacing, I is the current applied through two inner probes and V is the measure voltage.

The conductivities of PMWCNT and OMWCNT nanocomposite films are in the range of 10-4 S/cm, higher than that of Nafion and FMWCNT samples, this improvement might be attributed to the good dispersion observed with SEM in OMWCNTs composites.

Table 1: DC conductivity measurements of Nafion and its MWCNT nanocomposites

Samples	Nafion	N-P	N-O	N-F
σ (S/cm)	10^{-7}	10^{-4}	10^{-4}	10^{-7}

CONCLUSION

Nafion was modified by multiwalled-CNT using melt-mixing process. An increase in thermal stability was observed with the addition of 1 wt% of MWCNTs. Oxidation of MWCNTs improved the dispersion of thermal stability and mechanical properties of Nafion. An increase in electrical conductivity Nafion was observed when pure and oxidised MWCNTs were used as fillers. This suggests that the filler amount can still be reduced in order to avoid short circuiting the fuel cell.

By incorporating multi walled carbon nanotubes onto proton exchange membranes (PEM), its thermal stability is increased, making PEM fuel cells ideal for automotive applications.

ACKNOWLEDGEMENTS

Retha Rossouw, National Metrology Institute of South Africa (NMISA) is acknowledged for SEM measurements. This work has been supported by the National Centre for Nano-Structured Materials (NCNSM) at the CSIR and the Department of Science and Technology in South Africa.

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