

## Characteristic rheological responses of PVA solutions in water-containing solvents

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### 1. Introduction

Poly(vinyl alcohol) (PVA) is a semicrystalline polymer whose hydroxyl groups produce inter- and intramolecular hydrogen bonding. The extent of hydrogen bonding is greatly affected by stereoregularity of hydroxyl groups, so-called tacticity, of PVA[1~3]. Hydrogen bonding has a profound effect on the rheological and mechanical properties of the polymer, which is largely determined by the density and spatial arrangement of hydroxyl groups. Moreover, inter- or intra-molecular hydrogen bonding by hydroxyl groups may bring about complicated phenomena such as phase separation and gelation, which means the solution properties exhibit time-dependence. PVA solutions in water-containing solvents, such as dimethyl sulfoxide(DMSO)/water and NMMO hydrates, have a strong interaction between solvent and polymer.

In this paper rheological properties of PVA solutions in these solvent systems were investigated and discussed.

### 2. Experimental

#### 2-1 Materials

The degree of saponification of PVA (Aldrich Co.) was 99% and the weight-average degree of polymerization (DP) was 5,000. To make the mole ratio of water to the solvent the same, 80/20 by wt dimethyl sulfoxide(DMSO)/water and 86.7/13.3 by wt *N*-methyl morpholine *N*-oxide(NMMO)/H<sub>2</sub>O systems were chosen for the solvent of PVA.

#### 2-2 Viscosity measurement

Viscometric measurements were carried out using a dilution Ubbelohde viscometer which was immersed in a constant-temperature bath at 90 °C. The viscosity samples were prepared dissolving PVA was measured in DMSO/water and NMMO monohydrate.

#### 2-3 Rheological measurement

Dynamical mechanical measurements were carried out by ARES using a parallel-plate geometry, at a dynamic strain amplitude of 10% (gaps were 1 mm). Frequency sweep over 0.1 to 400 rad/s was performed at 90 °C.

### 3. Results and discussion

#### 3-1 Viscosity behavior

Figure 1 presents the logarithmic plot of  $[\eta]$  against molecular weight (Mw) at 90 °C for PVA solutions in DMSO/water and NMMO monohydrate according to the Mark-Houwink equation. The greater value of for DMSO/water than NMMO monohydrate suggests that the hydrodynamic volume of PVA molecule is larger in DMSO/water than in NMMO

monohydrate.

### 3-3 Rheological properties

Both systems exhibit non-Newtonian flow behavior, which is more noticeable with PVA/DMSO/water system. (Figure 2). Viscosity is increased with increasing concentration and its dependence on concentration is greater in NMMO monohydrate. The former system gives much lower values of power-law index and much greater low-frequency viscosity than the latter system. In consequence, the PVA/DMSO/water system becomes heterogeneous and shows a yield behavior.

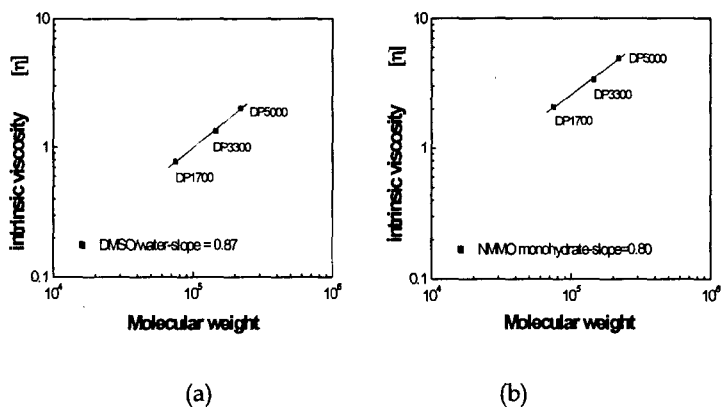


Figure 1. Plot of intrinsic viscosity against molecular weight at 90°C PVA/DMSO/water solution (b) PVA/NMMO monohydrate solution.

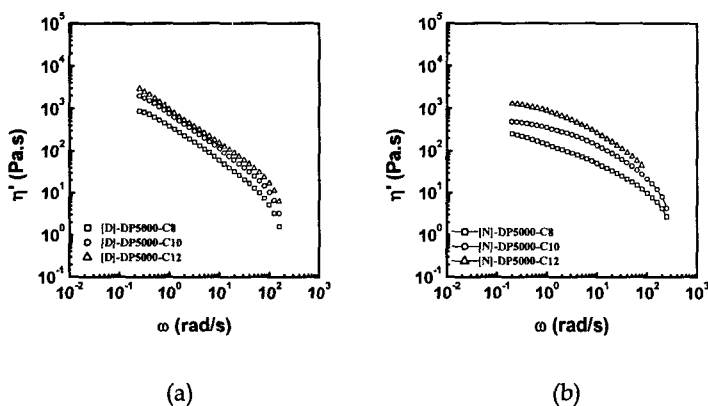


Figure 2. Dynamic viscosity curve of PVA solutions at 90 °C at several concentrations : (a) in DMSO/water solvent (b) in NMMO monohydrate solvent.

## 4. References

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