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Comparison of the Properties of Molecular Composites
Blends of Poly(vinyl alcohol)/Conducting Polymer

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1. Introduction

Conductive polymers(CPs) are a relatively new class of organic materials displaying as their foremost property a high conductivity combined with very light weight, flexibility and reasonably facile processability[1]. Due to their high conductivity/weight ratio, they have recently evinced much interest in potential application as EMI shielding screens, coatings or jackets for flexible conductors, rechargeable batteries and as possible substitutes for metallic conductors or semiconductors in wide variety of electrical devices[2]. Potential advantage of conductive or semi-conductive polymers lie in their light weight and in the versatility with which their synthesis and fabrication can be accomplished[3].

Polypyrrole(PPy) and polyaniline(PAn) are conducting polymer which has attracted much attention because of its high stability under ambient conditions together with high electrical conductivity. However, these are insoluble in any solvents and nonfusible even by heating up to the decomposition temperature and has poor physical properties[4]. To improve the mechanical properties and processability many kinds of method have been used, including the introduction of long alkyl groups into the main chain, the synthesis of soluble precursors, the preparation of conduction polymer composites, and so on[5]. Among these methods, the preparation of composites and blends are the easier and more effective and the combination of conventional polymers with conductive polymers or fillers allow us to create new polymeric materials with unique electrical properties.

In this work, conducting molecular composites and blends of poly(vinyl alcohol)

/polypyrrole(PVA/PPy)and poly(vinylalcohol)/polyaniline(PVA/PAn) were prepared. The morphology, antistatic property, and thermal properties of the composite and blend films were compared.

2. Experimental

2.1 Materials

Pyrrole(Fluka) and aniline(Aldrich) monomer were purified by distillation under reduced pressure. Iron(III) chloried anhydrous(Fluka), ammonium peroxodisulfate, methyl alcohol(Aldrich) and toluene(Aldrich) were used without further purification. Poly(vinyl alcohol)(PVA, Aldich) with an molecular weight of 31,000-50,000 was used as a polymeric matrix.

Ppy was synthesized chemically at 0℃ in a water/methanol(2.5 vol/vol) solution of $FeCl_3$. The pyrrole solution was added gradually onto the oxidant solution and then stirred mixture at 0℃ for 4 hours. PAn was synthesized by same method, using $(NH_4)_2S_2O_8$ as oxident agent and HCl as solvent. The resultant products were filtered, washed thoroughly with water and methanol and dried at 50℃ for 6 hours. Mean particle size of synthesized PPy and PAn powder were 4.11μm and 4.30μm, respectively.

2.2 Preparation of PVA/PPy and PVA/PAn composites

PVA/PPy and PVA/PAn composite films were prepared by chemical oxidative polymerization of pyrrole, which is similar to the procedure elsewhere [4,5]. PVA powders were dissolved in water and then $FeCl_3$ or $(NH_4)_2S_2O_8$ added. PPy and PAn were dissolved in toluene and HCl, respectively and inserted dropwise under vigorous stirring. All compounds were stirred at 0℃ for 5 hours, and then prepared composites were dried in a vacuum oven at 50℃ for 24 hours.

2.3 Preparation of PVA/PPy and PVA/PAn blends

To investigate the effect of processing on properties of PVA chemically modified by PPy and PAn, the blends were also prepared by direct polymer blends method. PVA powders were dissolved in water and chemically synthesized PPy or PAn added to solution. All compounds were mixing for few hours, and then dried in vacuum oven at 50℃ for 24 hours.

2.4 Characterization

Thermal degradation studies were performed under nitrogen using a TG 2950(TAcompany) at a linear heating rate of 10℃/min from room temperature at 600℃. Thermal behavior were determined by differential scanning calorimetry (DSC, SSC/5200H MII, Seiko Ins.) under nitrogen purging with a heating rate of 10℃/min. The microstructure of pure PVA, PVA/PPy systems, and PVA/PAn systems were studied by SEM. The antistatic properties of prepared samples

were investigated by Static Honestometer(Shishido co. Ltd.).

3. Results and Discussion

The sample code and wt% of component for composites and blends of PVA/PPy and PVA/PAn systems, and their thermogravimetric analysis results were are shown in Table I. For both two systems, the thermal degradation temperatures were commonly increased with increasing the content of conducting materials PPy and PAn. The degradation temperatures of composites were higher than those of blends at the same wt% of conducting materials.

Figure 1 shows the DSC curves of PVA/PAn system samples. For both two system, the melting peaks shifted to lower temperature as the content of conducting materials PPy and PAn increased. However, the shift of composites were higher than those of blends at the same wt% of conducting materials. When the content of conducting material was in the range of 0.5-1 wt%, two melting peaks were appeared indicating the presence of a complex phase in the crystalline region. The composites have also better conductivity and mechanical properties than blend at the same content of conducting materials (these data were not present here). Scanning electron microscope studies were carried out to compare the morphology of composite and blend. Figure 2 shows typical SEM of (a)pure PVA, (b)PVA/PPy composite and (c)PVA/PPy blend. The composite had the almost same smooth morphology as pure PVA indicating the molecular level dispersion of PPy in the matrix PVA. However, the aggregation particles of PPy in blend sample was observed showing the occurrence of phase separation between PVA and PPy.

The higher increase and shift of composites compared to blends may be attributed to the molecular level distribution of conducting materials PPy and PAn in matrix PVA in which induced the higher interaction energy between PVA and conducting polymer.

5. References

[1] Prasanna C., Conducting Polymers, Fundamentals and Applications, A Practical Approach, Kluwer Academic Publichers, 1999.
[2] Jiping Y., Yujing Y., jianan H., Xian Z., Wei Zhu and Mao X., (1996), *Polymer*, **37**, 5, 793-798.
[3] Ruckenstein E., Park J. S., (1991), *J. Appl. Polym, Sci.,* **42**, 925-934.
[4] Nakata M., Taga M., Kise H., (1992), *ibid*, **24**, 5, 437-441.
[5] Omastova M., Chodak I., Pionteck J., (1999), *ibid*, **102**, 1251-1252.

Table I. The sample code and wt% of component for composites and blends of PVA/ PPy and PVA/PAn systems, and their thermogravimetric analysis results

Sample code	PVA/Pyrrole (wt%)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue(wt%) at 570°C	Sample code	PVA/Aniline (wt%)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residue(wt%) at 570°C
PVA	100.0/0.0	287.9	311.9	10.6					
Ppy	0.0/100.0	225.7	-	70.4	**Pani**	0.0/100.0	247.6	-	53.2
Composite					**Composite**				
CP-1	99.9/0.1	328.5	359.8	23.7	CA-1	99.9/0.1	355.1	425.6	20.6
CP-2	99.5/0.5	252.7	494.6	43.8	CA-2	99.5/0.5	251.8	482.9	24.1
CP-3	99.0/1.0	243.5	541.6	45.4	CA-3	99.0/1.0	245.5	482.8	27.9
CP-4	97.0/3.0	209.4	-	65.6	CA-4	97.0/3.0	227.1	461.4	33.1
Blend					**Blend**				
BP-1	99.9/0.1	334.9	436.3	13.3	BA-1	99.9/0.1	291.6	315.1	15.0
BP-2	99.5/0.5	341.2	433.7	14.4	BA-2	99.5/0.5	299.3	323.3	15.5
BP-3	99.0/1.0	365.0	446.3	21.8	BA-3	99.0/1.0	294.1	323.6	17.1
BP-4	97.0/3.0	384.2	537.4	44.2	BA-4	97.0/3.0	306.4	400.5	20.5

T 10% : the temperature at which 10% weight loss has occurred.
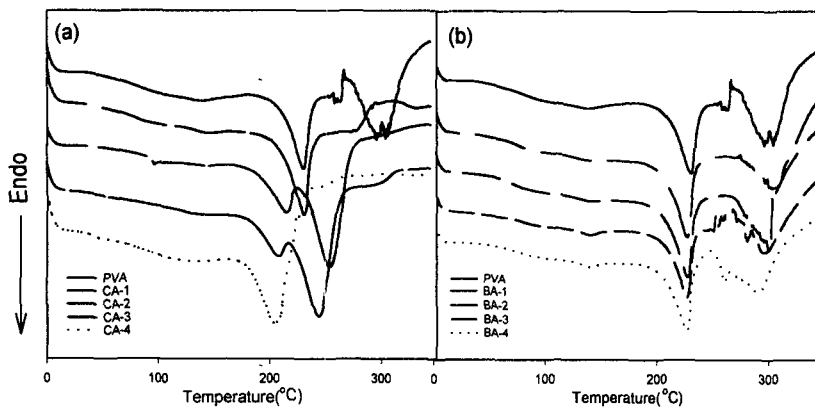T 50% : the temperature at which 50% weight loss has occurred.

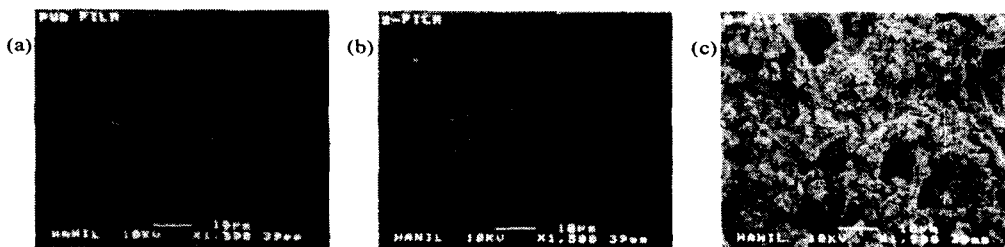**Figure.1 DSC curves for (a)PVA/PAn composites and (b)PVA/PAn blends.**

Figure.2 SEM of the (a)PVA, (b)PVA/PPycomposite CP-1 and (c)PVA/PPyb